PREPARATION AND CHARACTERIZATION OF LOW COST CrO_2 PARTICLES FOR USE IN HI-FI MAGNETIC RECORDING

By

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PREPARATION AND CHARACTERIZATION OF LOW COST CrO_2 PARTICLES FOR USE IN HI-FI MAGNETIC RECORDING

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CERTIFICATE

Certified that this work entitled 'Preparation and characterization of low cost CrO_2 Particles for use in Hi-Fi Magnetic Recording' by N. Thangaraj has been carried out under our supervision and that it has not been submitted elsewhere for a degree.

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ABSTRACT

In this work, low pressure methods of preparing relatively pure CrO_2 of the right particle - size and shape to meet the criteria of high-fidelity magnetic recording have been explored. In particular, CrO_3 and KNO_3 were heated together in a specially fabricated mild steel tube, first in the absence of and subsequently in the presence of additives Sb_2O_3 (1% by wt), Fe, Co, Ni (5% by wt each). The structure and morphology of the products were characterized by X-ray diffraction and electron microscopy, respectively. Estimates of the yield of CrO_2 in each of these preparations were made by DTA, TG and DTG analysis. The magnetic properties, namely, coercivity (H_c), saturation magnetization (σ_s) remanence magnetization (σ_r) and Curie temperature (T_c) were measured for all the prepared samples by using a vibration sample magnetometer.

From the results, it was concluded that acicular shaped CrO_2 was found in all the methods used, alongwith formation of Cr_2O_3 phase. The maximum yield of CrO_2 was found for the case of 5% Cobalt additive. The presence of additives generally reduced the particle size of CrO_2. The magnetic measurements revealed that the decreased particle size led to enhanced H_c . Curie temperature

measurements showed that the presence of 5% Fe increased the T_c from 128° C to 150° C, and presence of 1% Sb_2O_3 and 5% Co decreased T_c from 128° C to 125° C and 123°C, respectively.

The use of a stainless steel or a coated mild steel container, as well as variation in batch composition and temperature are suggested as possible ways of minimizing the Cr_2O_3 phase and thereby optimizing the yield of CrO_2.

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CHAPTER I

INTRODUCTION

1.1 PREVIEW OF THE PROBLEM

The commercial importance of magnetic tapes has increased considerably in the last ten years. Numerous studies have been under taken as much in the area of research for new ferri- or ferromagnetic materials as on their preparation.

For magnetic recording it is necessary to obtain a coercive field greater than 300 Oe and a demagnetizing factor $\frac{\sigma_r}{\sigma_s}$ (σ_r - remanant magnetization, σ_s - saturation magnetization) between .3 and .5 for a random assembly of 'acicular' or needle like particles. The most suitable materials for this purpose are commonly needle- like particles. Three type of materials have been mainly used: (i) metallic particles, (ii) Gamma Iron Oxide, (iii) Chromium dioxide.

Since finely divided metallic particles are very pyrophoric, and γ- Fe_2O_3 particles can not be used for high frequency applications, their use is very limited. Even though Co-doped γ- Fe_2O_3 can attain coercive fields of the order of 600 Oe, the strong thermal dependence of its magnetic characteristics has led to the choice of CrO_2 which has excellent magnetic characteristics necessary for magnetic

recording. Since all the major processing methods of Chromium dioxide involve high cost mainly because of high pressure involvement in the preparation, relatively low cost methods for the preparation of CrO_2 would be necessary to ease the commercialization of the product. Such methods have been explored in the present study, and the product has been characterized by a variety of measurements with a view to its use in Hi-Fi magnetic recording.

1.2 PRINCIPLES OF MAGNETIC RECORDING

Magnetic materials have attained a prominent position in the fields of audio, video, and digital recording by virtue of their reliability, economy and ease of usage. Information is stored as a passive condition of the medium and once stored, is usually unaffected by the environment. Yet the information can be erased when required, and the same surface used to make another recording; the process is apparently infinitely reversible.

In the magnetic recording technique, a high permeability magnetic core made of Mumetal laminations or ferrite blocks and having a narrow air gap (25 μm) is magnetized by passing the input signal current through a coil of wire wrapped around the core. The magnetic field in crossing the air gap extends beyond the core and penetrates the

recording surface. As the surface moves away from the writing gap, some demagnetization occurs, and the coercivity, H_c, of the magnetic recording material must be high enough to ensure that sufficient flux remains around each magnetized region to affect the reading head. The reading head is similar in structure to the recording head, and its function is based on the fact that, for some flux lines, the path through the core has a lower reluctance than the path across the air gap. Thus, as a changing magnetic pattern moves past the gap, changing flux exists in the core and a signal is observed in the pickup coil. As the wavelength of the recorded pattern decreases, or as the separation between the tape, say, and the head increases, the inequality between the two reluctances (core path Vs air-gap path) is less likely be true. Less flux follows the core path, and the output signal decreases. Usually, for reasons of convenience, the relative motion is achieved by moving the recording medium past a stationary head (or heads). Occasionally the situation is reversed. For example, as in the case of some video recorders, both head and medium are in motion. Recording applications fall into two categories, analog and digital.

1.2.1 ANALOG RECORDING

This type of recording is found in audio, video, or instrumentation applications. Here, the output signal

should contain large signal- to- noise ratio, and it must be linearly related to the input signal. The latter implies that, despite the obvious non-linearities of the magnetization curves and the spatial distribution of the writing head field, the magnetization intensity (I_s) in the medium must be proportional to the applied field. The linearity is achieved by superimposing on the signal field an ac bias field whose frequency is about 5 times that of the highest signal frequency. This results in "anhysteretic" magnetization (for a detailed description of this term, see reference)[1]. This model treats the simultaneous application to the recording surface of a constant dc field and an ac field whose amplitude is initially large and then reduced to zero. The anhysteretic remanent intensity is found to be proportional to the dc field regardless of the previous magnetic history of the medium, provided that the remanent intensity $I_r \leqslant \frac{1}{2} I_{rs}$ the maximum remanent intensity. The real situation is somewhat different, since during the recording process, the dc field is neither constant in magnitude nor in direction. Essentially the bias field alone creates in the moving medium a series of partly overlapping cylinders of alternately directed magnetization. The addition of a lower frequency signal field results in asymmetry in the in the volumes of adjacent cylinders so that different regions are magnetized to different depths, depending on

the amplitude of the signal field. Distortion of the signal results if the amplitude of the bias field is too large or too small. Noise is also of great concern in analog recordings and exists as random unrelated impulses (background noise), unwanted signals (e.g., 'print through' between adjacent layers in a reel of tape), or random variations of the desired signal (dc noise and modulation noise).

1.2.2 DIGITAL RECORDING

In this method, which is the one adopted by the computer industry, information is first coded into binary form. Then, as each unit of information is either a binary ONE or ZERO, only two states of magnetization are needed, usually magnetic saturation in two opposite directions. Linearity of magnetization with field is quite unimportant here, but it is important that the magnetization should change from $+ I_r$ to $- I_r$ in a very small distance if good pulse resolution at high densities is to be achieved. The width of the transition region is a function of the head field gradient (near $H = H_c$), the shape of the hysteresis loop, and the geometry of the magnetized regions. High values of write current, high values of I_r , high recording densities, and low coercivity (H_c) all tend to produce broad transitions which lead to broad and possibly overlapping

pulses in the reading head. These can result in a displacement of the time position of the pulses and, therefore, in errors in the read back data, and must therefore be avoided.

1.3 CHARACTERISTICS OF MAGNETIC MATERIALS AS RECORDING MEDIA

In considering the magnetic properties of materials for use in recording surfaces, one looks for (1) coercivities between 250 - 750 Oe: high coercivity generally means high output and narrow pulses, but coercivities $>$ 1000 Oe are usually beyond the switching capability of today's writing heads; (2) high remanent intensities: again, to provide high output, although at high densities, the demagnetization fields may become undesirably high; and (3) particles or crystallites which are small,(essentially these features help in reducing 'noise' while recording) single domains of very uniform shape and size.

For all tape recording materials, the recording performance is controlled by the following magnetic and structural characteristics.

1.3.1 COERCIVITY

Since coercivity, H_c, is the magnetic force retained by the material in the absence of an applied field, it is

a measure of magnetization field necessary to record or erase the signals stored on a magnetic tape. The typical values of 'H_c' are in the range of 250-300 Oe for known recording materials. High coercivity gives rise to high output signals and a narrow pulse. The coercivity values greater than 1000 Oe are usually beyond the practical use since it is necessary to have high field strength to erase the signals and also high bias current which can not be provided by the recording heads. Low coercivity is characterized by poor frequency response.

Coercivity is a linear addition of two terms (i) local effects due to magneto-crystalline anisotropy which is because of the existence of preferred stable magnetization with respect to crystal axes. (ii) The effect of magnetostatic fields, arising from growth morphology and particle interaction known as shape anisotropy. The high crystalline anisotropy renders the magnetization harder-to-rotate away from the preferred magnetization direction, and hence to higher coercivity. Hence coercivity depends upon the nature of particle size and shape.

1.3.2 REMANENCE

High remanent magnetization gives rise to high output and it is normally between 1500-2000 Gauss. The retentivity of the medium is a measure of magneto-motive force available

in a certain material to produce signal output. Hence it is desirable to use as recording medium,a material having high remanance magnetization. The shape of demagnetization may be more important than retentivity values especially where short wavelengths are to be recorded. The remanence intensity of fine particles largely depends on the number of preferred axes of magnetization and the saturation flux density (B_s) of the material. If there is only one preferred axis, as in the case of acicular particles where shape anisotropy dominates, the chances are less in randomly oriented samples of coincidence between the direction of applied field and preferred direction and hence the retentivity is less. But it can be made higher by orienting the particles in the direction of the applied field. Theoretically, remanence field (B_r) would be equal to B_s for perfectly oriented particles measured in applied field direction and $B_r = 0$ measured in a direction perpendicular to that of the applied field.

1.3.3 PARTICLE SIZE [1,2]

The coercivity and remanence magnetization both strongly depend upon particle size. As particle diameter of the magnetic material decreases, the intrinsic coercive force (H_{ci}) and remanence ratio (B_r/B_{is}) increases rapidly as single domain size is approached. The increase in coercivity is associated with the progressive removal

of domain boundaries and domain reversal nucleii. When particle size is reduced to single domain size, their coercive force can be understood in terms of resistance to domain rotation imposed by anisotropy. If the particle size is further reduced to a critical size below which thermally activated magnetization reversal occurs which causes H_{ci} and B_r/B_{is} to decrease to zero, the behaviour is called superparamagnetism.

In multi domain particles, the domains are separated by microscopic regions, known as domain walls. In ferromagnetic materials, the magnetization of single domain is not zero. But the net magnetization is zero since domains are oriented randomly.

The domain wall energy[3] is made up of two types of energies such that exchange and anisotropy energy.

$$\sigma_w = \sigma_{\text{exchange energy}} + \sigma_{\text{anisotropy energy}}$$

$$= \frac{\pi^2 J S^2}{Kt} + Kt$$

Where σ_w = Total domain wall energy in ergs/cm^2.

J = Exchange integral

S = Atomic spin

K = Crystalline anisotropy constant

and t = Domain wall thickness

When t becomes very small, of the order of $10^{-4} - 10^{-5}$ cm, $\sigma_{exchange}$ becomes very large and $\sigma_{anisotropy}$ is almost negligible, then

$$\sigma_w = \frac{\pi^2 J S^2}{Kt}$$ which makes particles unstable.

In single domain particles, the coercivity is determined by the crystal anisotropy. The energy of material will be comparatively low which leads to minimum energy state. Hence, it is concluded that the single domain particles have the lowest energy state and so have the larger value of coercivity and remanence. For random orientation of particles containing cubic anisotropy, the coercive force is given by:

$$H_c = 0.64 \ K_1/I_s$$

Where K_1 = Anisotropy constant

I_s = Intensity of saturation magnetization

Darnell[4] calculated the critical upper size for single- domain behaviour of CrO_2 by the method used for γ- Fe_2O_3 particles. He found from his magnetic measurements that CrO_2 particles having diameter less than 0.2 μm and axial ratios of 5:1 show single domain behaviour.

1.3.4 PARTICLE SHAPE[5]

The particles must be small single domain of very uniform shape and size to reduce the noise. The coercive force of a single domain particle has a high value since the magnetization changes occur through the usual high field process of rotation of the total magnetic moment of particle. The rotation process is controlled by the effective anisotropy of particle like magnetocrystalline anisotropy, strain anisotropy and shape anisotropy. If an elongated particle is idealized in the shape of a prolate ellipsoid whose major axis coincides with the applied field direction, the coercive force may be written as,

$$H_c = (N_b - N_o) I_s$$

Where I_s = Intensity of saturation magnetization

N_o & N_b = The demagnetizing factors of ellipsoid along the major and minor axes, respectively.

In the case of elongated particles $(N_b - N_o) = 2\pi$

so $H_c = 2\pi I_s$.

In the case of spherical particles

$$H_c = 0.48 \, I_s$$

The coercivity for a random assembly is given by **Stoner** et al[6]

$$H_c = 0.479 \, (N_b - N_o) \, I_s$$

And, remanent intensity of magnetization

$$I_r = \frac{1}{2} I_s .$$

Thus the coercivity depends upon particle size as well as its shape.

The critical fields are due to a linear addition of (1) the local effect of crystalline anisotropy 'K' and (2) the effect of shape anisotropy .

Thus the coercivity is given by Eagle et al[7]

$$H_c = \alpha M + B\ (K/M)$$

Where α = the shape factor, B = constant.

Non uniform reversal models suggest that α is dependent on shape as well as on size which is given by

$$\alpha = KR_0\ R^{-2} - N_{11}$$

Where N_{11} is the major axis demagnetizing factor and K is a dimensionless factor of order unity.

1.4 A COMPARATIVE REVIEW OF THE MORE IMPORTANT TAPE-RECORDING MATERIALS

A number of magnetic materials which have the above-mentioned properties have been tried as potential media for tape recording. Out of these, a few are compared and catalogued below.

1.4.1 METALLIC PARTICLES[8]

Metallic particles can be used advantageously in recording surfaces since their higher saturation magnetization leads to higher output signals at low recording densities when compared with oxide particles having the same volume packing fraction. Finely divided particles of iron, cobalt and nickel and their alloys are used for magnetic recording. However, there is a considerable danger in using these metallic particles as recording media since these finely divided metallic particles are liable to burn spontaneously on exposure to the atmosphere. So a protective coating must be given to prevent this oxidation. But this protective coating will affect the recording performance of the metallic particles considerably.

1.4.2 MAGNETITE (Fe_3O_4)[8]

Single domain particles of magnetite may be prepared by the process developed for $\gamma - Fe_2O_3$. Magnetite has the typical inverse spinel structure and its magnetic moment is 4 Bohr magnetons. Even though it has magnetic properties some what superior to $\gamma - Fe_2O_3$, it was neglected because of the following reasons:

(i) The magnetocrystalline anisotropy constant of Fe_3O_4 is higher, and consequently, the coercivity

decreases more rapidly with increasing temperature than in the case of γ- Fe_2O_3 .

(ii) Easy oxidation of Fe_3O_4 to Fe_2O_3 leads to poor tape stability.

(iii) Because of higher value of coercivity, it needs higher bias current to write or erase.

(iv) 'Print-through' effect is more predominant in Fe_3O_4 than γ- Fe_2O_3 .

1.4.3 GAMMA IRON OXIDE (γ-Fe_2O_3)[1]

In the early days spherical particles of γ- Fe_2O_3 were used for recording purposes. Since it has low coercivity (80-120 Oe) , low remanence ($B_r \sim 400$ Gauss) and very low crystal anisotropy, they are of little use in the tape industry. Here particle size depends on the conditions of preparation.

In later years, these were replaced by acicular type of γ- Fe_2O_3 which have the coercivity value of 200- 400 Oe with remanence field around 500- 900 Gauss. These particles are prepared under a controlled oxidation of acicular Fe_3O_4 in the presence of moisture at 220-250° C.[9]

The persistent and widespread use of this material was only due to the non-availability of alternative materials

which could serve the same needs better. It has a pronounced tendency to agglomerate and form lumps in any dispersion media and this non- uniform distribution of material leads to improper alignment of particles on tapes, leading to fairly high noise levels. 'Print-through' effect is also severe in these tapes. Another serious drawback is its limitation to use at low frequencies only.

1.4.4 COBALT SUBSTITUTED IRON OXIDES (γ- $Fe_{2-x}Co_xO_3$)[10]

The problems associated with Fe_3O_4 and γ-Fe_2O_3 led to the development of Co- substituted iron oxides. These materials have the coercivity in the range of 400-1000 Oe which depends upon the Co - content. These oxides have very high magnetocrystalline anisotropy. They can be used at higher frequencies and have higher output and low peak shift. A typical Cobalt substituted iron oxides may be prepared by coprecipitating Co and Fe hydroxides from an alkaline solution of Ferric chloride and Cobaltous nitrate and heating the mixture to 130-170° C.

However, as these materials have high magneto-crystalline anistropy values, their coercivities are markedly sensitive to variation of temperature. Also, variations in the storage and operating temperatures may lead to some signal loss.

1.4.5 'AVILYN'[11]

'AVILYN' particle is an acicular magnetic iron oxide on whose surface certain Cobalt compounds have been adsorbed. The coercive force of the particles is determined by the amount of Cobalt and other preparational conditions and is controllable between 450- 800 Oe. Previously known Cobalt substituted iron oxide particles exihibited an undesirable degree of temperature sensitivity with respect to remanence and coercive field, while these 'AVILYN' particles display much improved thermal stability.

1.4.6 CHROMIUM DIOXIDE (CrO_2)[12]

The replacement of the abovementioned media such as γ- Fe_2O_3 , metallic materials etc. is taking place rapidly by acicular particles of CrO_2 since it has higher coercivity and retentivity as compared with others and have become very popular in the last few years with all the leading tape manufacturers. The magnetic properties of the recording materials are shown in Table 1.1.

The pronounced acicularity, high coercivity and smoothness of surface displayed by CrO_2 particles lead to the ease of dispersion and high orientation ratios. The principal advantages of chromium dioxide particles are that

Table 1.1

Magnetic Properties of the Recording Materials

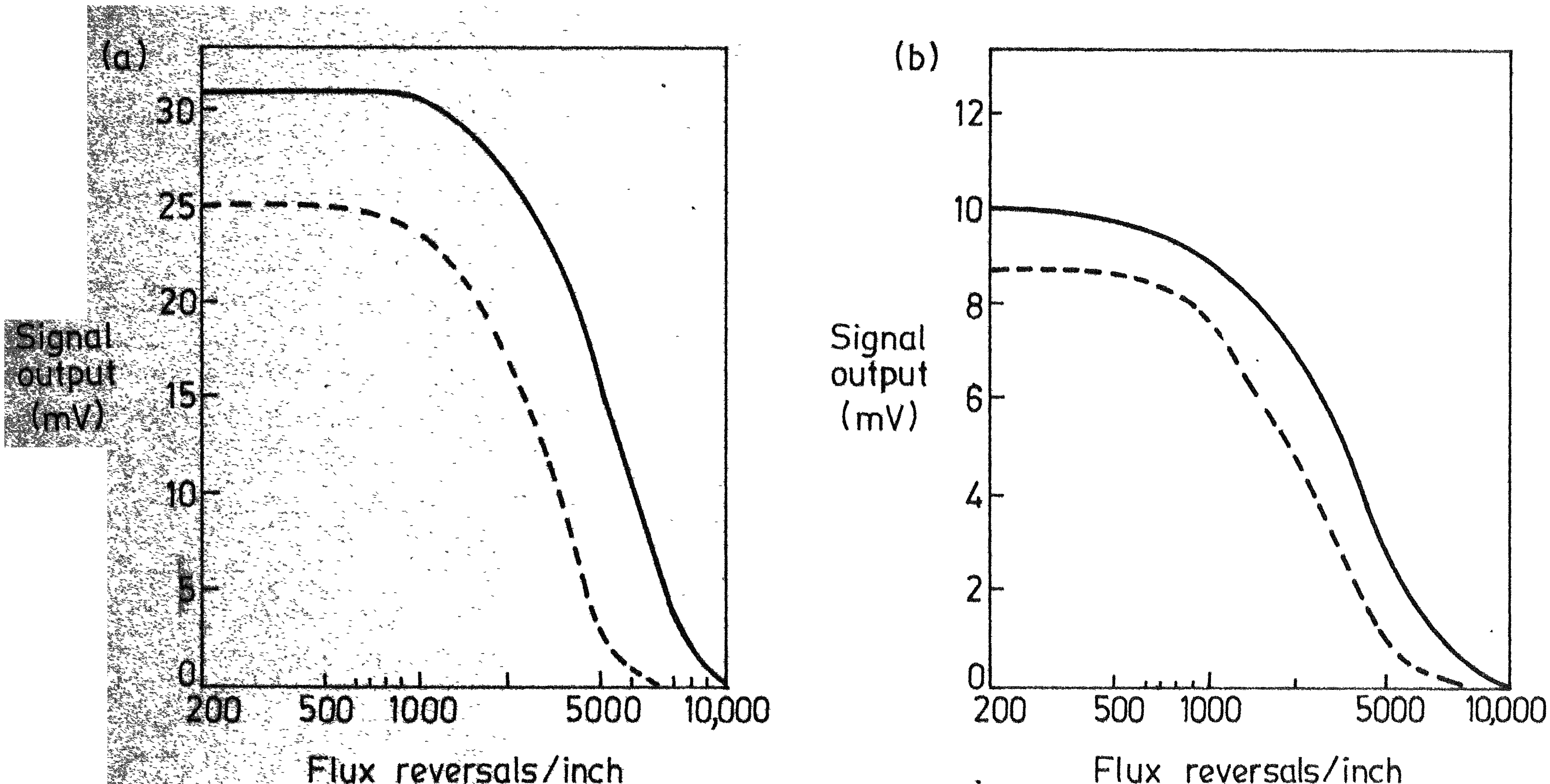
Magnetic Materials	Saturation Intensity of Magnetization (emu/gm)	Saturation Induction (I_s) (emu/cc)	Curie Temp. T_c (^oC)	Magneto-crystalline anisotropy K_I (ergs/cc)	Maximum coercivity H_c (Oe)	Maximum orientation ratio I_r/I_s (oriented)
				$\times 10^5$		
OXIDE PARTICLES						
γ-Fe_2O_3	74	400	590	-0.464	380	0.75
Fe_3O_4	84	478	575	-1.1	550	0.70
γ-$Fe_{2-x}Co_xO_3$						
x = 0.04	50	233	-	+10.0	400	0.70
x = 0.06	44	205	-	-	600	0.70
CrO_2	90	440	117	2.5	600	0.8 - 0.9
AVILYN	83.2	-	-	-	570	-
METAL PARTICLES						
Iron	159	1714	770	4.8	645	0.57
Iron - Cobalt	107	-	900	-	1000	0.90
Cobalt	150 - 200	1422	1070	43.0	900	0.83
METAL FILMS						
Iron	218	1700	770	4.8	800	0.95
76.2 Co-N_i-P	120	1100	-	-	1300	0.80

they can be made of uniform size and are free of dendrites. They are readily oriented and give excellent high density (short wavelength) recording performances.

The Curie temperature, T_c , of CrO_2 is much lower than that, for example, of γ- Fe_2O_3 (113.5° C of CrO_2 Versus 590° C of γ- Fe_2O_3). In fact, the temperature is so low as to cause concern that accidental erasure might result from a relatively modest increase in the ambient temperature during use, transportation, or storage. However, the dominant anisotropy appears to be that of shape, and thus the coercivity of the particles should be proportional to the intensity of magnetization. Consequently, an increase in temperature towards the Curie point will produce an equivalent decrease in magnetization and coercivity. That is, the balance between demagnetization field ($\propto M$) and the ability to resist demagnetization (H_c) will remain substantially unchanged, and no erasure will result (unless, of course, the temperature reaches the Curie point). The low Curie temperature property of CrO_2 is also utilized for thermomagnetic recording.

CrO_2 responds to much higher frequencies (upto 7 MHz) with a good signal output and a good resolution. Table 1.1 summarises the known magnetic properties of CrO_2 and γ-Fe_2O_3. From this Table we see that one should expect that a better recording surface could be made from CrO_2 particles than

γ- Fe_2O_3 particles, the higher moment density and orientation and greater coercivity imply larger output signals at low densities, and that the coercivity should also improve high density performance. Recording measurements in support of these experiments were reported by Speliotis[13] who compared the performance of γ- Fe_2O_3 and CrO_2 tapes. The density response curves for the two tapes are shown in Fig. 1.1. In one case, the head used had a writing gap of 500 μin and a reading gap of 250 μin, and in the other the gaps were both 90 μin. We notice that, even though the CrO_2 tape in thinner, its output at low densities is appreciably higher than that of the iron oxide tape with either head. At the higher densities, of course, the thinness of the CrO_2 tape helps the resolution, and thus the output. Hence, CrO_2 is the first choice as a video tape material. It has low noise, low 'Print-through', greater signal to noise (S/N) ratio than γ- Ferric Oxide and makes an ideal material for recording instruments. In computer tape-storage and tape recording, the superior properties of CrO_2 allow the same level of peak-to-peak amplitude of recording as γ- Fe_2O_3 at half the tape coating thickness. It also therefore means that larger number of bits of information can be stored on CrO_2 and with better resolution than hitherto possible with γ-Fe_2O_3 tapes. It is due to these merits that most of the manufact-



—— CrO_2

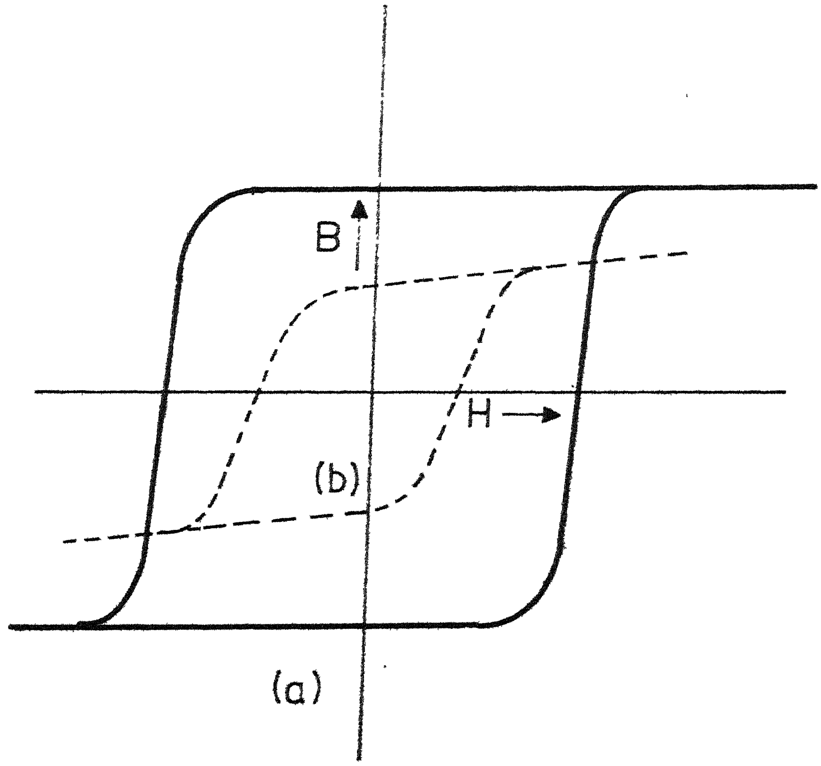
---- γFe_2O_3

$4\pi M_s$ gauss	H_c O_e	$\frac{M_r}{M_s}$	t μ inches
1440	465	91	285
860	299	76	500

Fig. 1.1

urers have incr^asingly favoured CrO_2 tapes.

Moreover, the most desired characteristics of a recording material are that (i) the assembly of magnetic particles has single domain regions whose direction of easy magnetization coincides with that of the applied field and (ii) that each of the regions have the same field requirement for an irreversible change in magnetization. Despite the slight uncertainty[14,15,16,17] about the direction of magnetocrystalline easy axis with respect to the long axis of the particles, there is no doubt about the uniaxial nature of the resultant anisotropy. Consequently we expect for a random assembly of particles, a value of squareness ($S = M_r/M_s$) of .5 . In addition to being highly acicular particles of chromium dioxide show no dendrites in the electron microscope and are relatively easy to disperse and to align in a magnetic field. Value of $S = 0.82$ are not un-common. Fig. 1.2[18] which compares the hysteresis traces of CrO_2 and $\gamma - Fe_2O_3$ on tape, clearly demonstrates that the second requirement above is better achieved for CrO_2 than for $\gamma - Fe_2O_3$. The superior squareness of the hysteresis trace of CrO_2 tape sample is attributed to the condition that most of the single domain regions have nearly the same critical field. The small range of critical field correlates well with the small range in particle size and indicates that the spread in values



Hysteresis trace of CrO_2 on tape, B = 1000 G/cm H = 250 Oe/cm.

Hysteresis trace of γ - Fe_2O_3 on tape, B = 1000 G/cm H = 250 Oe/cm.

Fig. 1.2

of particle coercivity is small. This property of a recording medium is desirable because it indicates an ability to resist the effects of self magnetization found in high bit density recordings.

The disadvantages of CrO_2 particles are that they are less stable than $\gamma - Fe_2O_3$, they require surface treatment to reduce time dependent changes in their magnetic properties, and that they are abrasive to the read- write heads. The latter property stems from their inherently greater hardness and from the way in which the particles fracture. However, use of the proper binder material can minimize this defect. Indeed, use of binders may even be turned to advantage as a method of preventing the accumulation of adhesive debris on the surface of the head.

1.5 EARLIER PREPARATIVE HISTORY OF CrO_2

As for back as 1828, Wohler[19] found that thermal decomposition of CrO_2Cl_2 gave oxides of chromium in which one of the oxide had ferromagnetic property. Actually CrO_2 forms along with other oxides of chromium like Cr_3O_8, Cr_2O_5, and Cr_2O_3. In 1861, Geuther[20] found that thermal decomposition of CrO_3 also gave products having ferromagnetic property and supposed the material to be $CrO_3 . 2\,Cr_2O_3$.

Schukoff[21] in 1908 reported that thermal decomposition of CrO_3 at 500-510° C gave a ferromagnetic oxide of chromium with a chemical formula $2\ CrO_3 \cdot Cr_2O_3$. Honda et al[22] studied the thermal decomposition of CrO_3 by thermobalance and reported two intermediate products of composition Cr_6O_5 and Cr_5O_9. Michel and Benard[23,24] showed that the decomposition of CrO_2Cl_2 yielded about 50% of CrO_2 along with Cr_2O_3 and that the chromium dioxide was ferromagnetic. Subsequent to this work, a number of literature references are available for the preparation, physical and chemical properties, and applications of CrO_2.

1.6 PREPARATION OF CrO_2 PARTICLES

1.6.1 AT ATMOSPHERIC PRESSURE

It would clearly be an advantage to have a preparation method which could be carried out at atmospheric pressure. Such methods have been described by Michel and Benard and Schwartz et al[25] who synthesised CrO_2 by dechlorination of CrO_2Cl_2 and by deoxygenation of CrO_3 respectively. The products obtained in these cases were found to be contaminated with Cr_2O_3. This was explained by Roy[26], Kawai and Sawaoka[27] who proposed that CrO_2 is a metastable phase at room temperature, and that high pressure is required to prepare it in pure form. The phase diagram of chromium-

oxygen system proposed by the above investigators is shown in Fig. 1.3. However, Darnell[28] prepared CrO_2 particles by vapour deposition from chromyl chloride. Also Cox[29] used CrO_2 particles as seeds and increased the yield of chromium dioxide in the decomposition of the chromyl chloride to about 90%. In 1968, Hicks and Jacobson[30] prepared pure CrO_2 of low coercivity at 250-375^{o} C at pressure no greater than one atmosphere. They were continuously introducing a mild reducing agent NO (nitric oxide) into the reaction chamber containing CrO_3 and calculated amounts of modifying agent such as Sb_2O_3. The unreacted gases were removed continuously from the reaction chamber and then they had recovered the ferro-magnetic chromium dioxide formed. It was found that decomposition of CrO_3 results in lower oxides of chromium below the tetrapositive valance state and it was difficult to control the decomposition to result in exactly tetra-positive valance state. However, in the presence of a mild reducing agent like NO, this decomposition could be controlled such that large quantities of chromium dioxide were obtainable at low pressures. Hirota et al[31] and Sugimori[32] found that heating of CrO_3 in air with hydrogen peroxide results in ferromagnetic CrO_2. Fukuda[33] was also able to prepare CrO_2 particles at atmospheric pressure by dissolving CrO_3 and potassium nitrate in water and heating

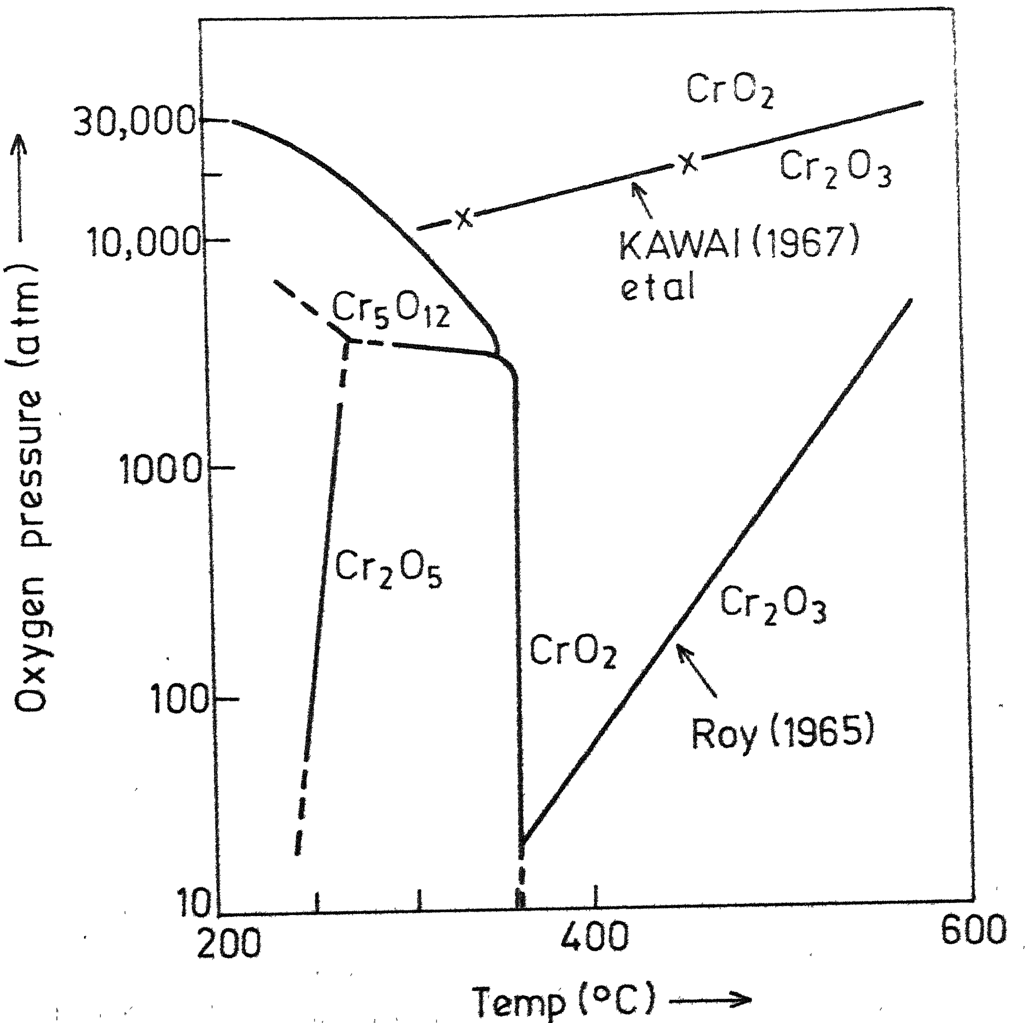


Fig. 1.3. Phase diagram of the Chromium-Oxygen system.

the mixture after drying, at 415° C for 45 minutes. Shimotsukasa[34] added to CrO_3 solution a concentrated solution of nitric acid and oxalic acid in order to reduce about two-thirds of the Cr^{6+} to Cr^{3+}. The solution was dried and the residue was heated at 330° C for 4 hours under an atmosphere whose oxygen partial pressure was very carefully controlled, to give CrO_2.

1.6.2 AT HIGH PRESSURES

Two methods of preparation of CrO_2 particles can be considered at high pressures such as: (i) Reduction of chromium having a degree of oxidation greater than 4+. (ii) Oxidation of chromium 3+ or metallic chromium.

Most of the methods have been concerned with the reduction of higher oxides of chromium such as CrO_3 and few of them having used oxidation of lower oxides of chromium such as Cr_2O_3 under high pressures. Some of the methods are described here.

Ariya et al[35] prepared pure CrO_2 by heating anhydrous CrO_3 under an oxygen pressure 300 atmospheres at 420° C to 450° C and studied the chemical and crystallographic properties of CrO_2. Here the oxygen pressure resulted from the decomposition of CrO_3. Thamer et al[36] obtained CrO_2 by the hydrothermal decomposition of CrO_3 under water

vapour pressures and temperatures ranging from 300° C to 325° C.

Shibaski et al[37] prepared CrO_2 by the oxidation of $Cr(OH)_3$ under high oxygen pressure. Amorphous $Cr(OH)_3$ was treated in oxygen at high temperature and pressure upto 2100 bars. In the temperature range from 180° C to 350° C, CrOOH was obtained. At 400° C and 80 bars or at 800° C and 1500 bars CrO_2 crystallized. A more efficient method was described by Uchino et al[38] and consisted of heating the chromyl chloride with CrO_3 under oxygen in an autoclave at 350°C and a pressure of 80 to 204 Kg/Cm^2.

Very pure single- phase chromium dioxide was obtained by Swoboda et al[12] from the thermal decomposition of CrO_3 in the presence of water at high pressure. Equimolar quantities of CrO_3 and water were heated in a thin walled platinum container inside a pressure vessel at 400-525°C and 500-3000 Kg/Cm^2 for 5 -10 minutes. Oxygen produced by the reaction $CrO_3 \longrightarrow CrO_2 + \frac{1}{2} O_2$ was used to stabilize the CrO_2. The use of double vessel is common; the inner one is thin and made of platinum or glass which does not react with CrO_2 and the outer vessel is of stainless steel and thicker to withstand the high pressure. Terada et al[39] recommended the use of water (usually between 10 and 40% of the weight of CrO_3) to obtain CrO_2 of uniform quality. Platinum containers are most commonly used because of their

chemical inertness but Kubota et al[40] found that platinum antimony, and tellurium tend to reduce the grain size of CrO_2. The thermal decomposition of anhydrous CrO_3 was also used by Kubota[41,42] to obtain pure CrO_2 . A high pressure bomb made of Stainless steel with a Cu-gasket, was used as the container and a high pressure of oxygen was obtained by Oxygen liberated from the starting material CrO_3 during decomposition. The volume of the reaction chamber was 36 Cm^3 and the pressure was measured by a Bourden gauge set in the cap of the apparatus. The bomb containing the sample was heated in an electric furnace and the gauge was set out side the furnace. Kubota studied the electron micrographs of different oxides of chromium and showed an abnormal grain growth of CrO_2 during the decomposition of Cr_2O_5 to CrO_2 . The activation energies of the decomposition of Cr_2O_5 and CrO_2 to Cr_2O_3 in air are 61.7 and 48.2 K Cal/mole, respectively. From this we infer that CrO_2 is less stable than Cr_2O_5 . The pressure temperature diagram of various chromium oxides has been determined when CrO_3 undergoes decomposition. This is shown in Fig. 1.4.

In the diagram, two features are noteworthy. One is the horizontal 'plateau' regions belonging to the stable region of various oxides. The second is the vertical rising portions, which correspond to release of oxygen due

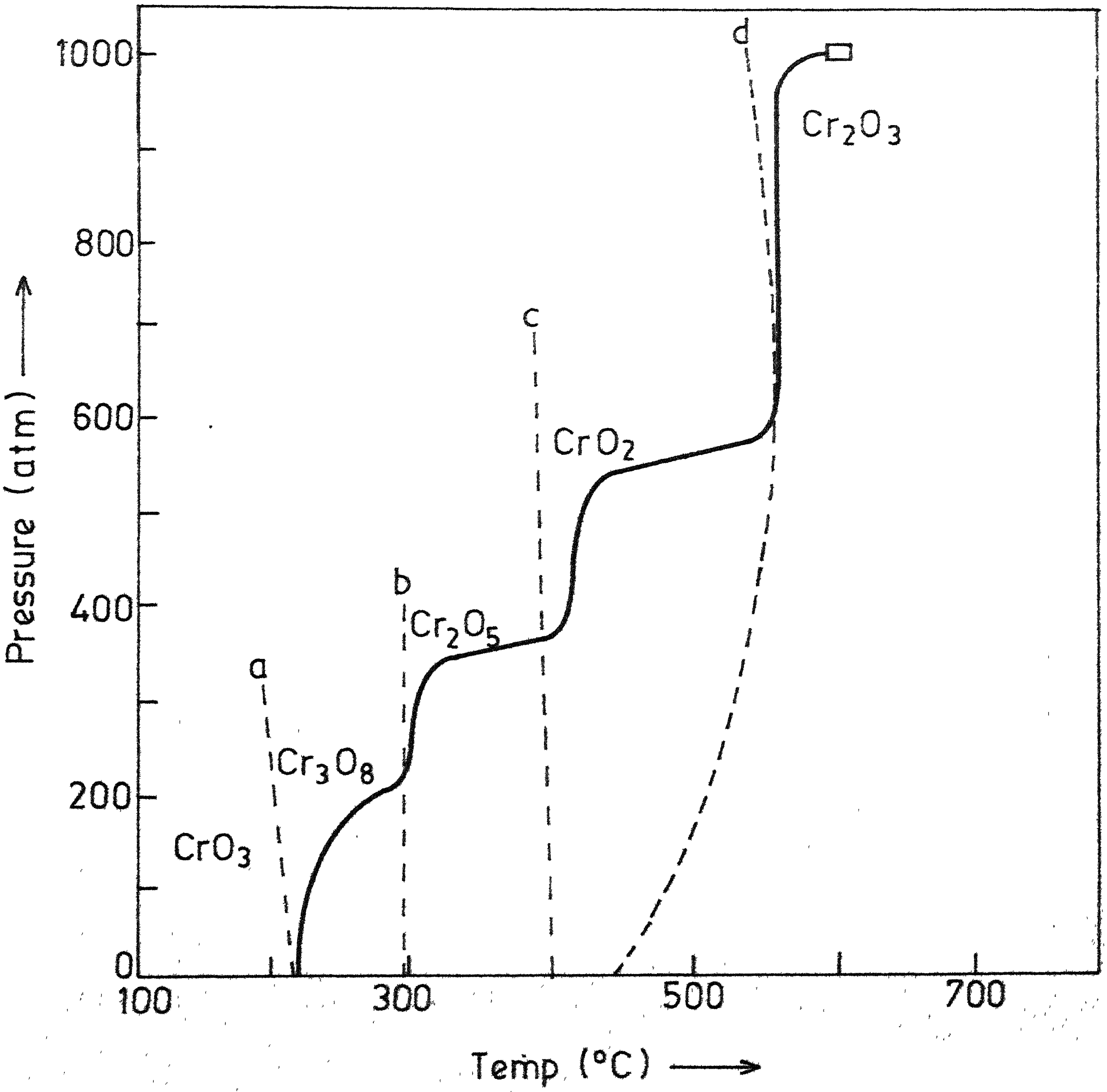


Fig. 1.4. Pressure temperature diagram of the thermal decomposition of CrO_3.

to decomposition of oxides. It is also seen that the transitions $CrO_3 - Cr_3O_8$, $Cr_3O_8 - Cr_2O_5$ and $Cr_2O_5 - CrO_2$ depends upon the temperature but not on the pressure in the gauge investigated. The transition temperatures are 220°C, 280° C, and 370° C respectively. The transition $CrO_2 - Cr_2O_3$ can expressed by a curve 'd' in the diagram which depends upon both the pressure and temperature.

The hydrothermal decomposition of CrO_3 is further described in a series of patents. The hydrothermal method of preparation of CrO_2 , in which Cr_3O_8, Cr_2O_5 or mixture of CrO_3 with $Cr(OH)_3$ or Cr_2O_3 are used as the starting compounds in the place of CrO_3 , are reported by Arthur and Ingraham[43] and Cox[44].

In Aug. 1977, Williston et al[45] developed an efficient method to produce CrO_2 based on Arthur's[46] and Cox's[44] work in which a reaction mixture comprising one or more chromium oxides (usually $CrO_3 + Cr_2O_3 + H_2O$) was used. The chromium has an average valance other than + 4 were heated in the presence of water to a temperature greater than 250° C (at 350° C) and a pressure of atleast 200 atmosphere (at 500 atmospheres). The resulting ferromagnetic CrO_2 particles were collected after cooling and drying.

Claude et al[47] heated CrO_3 with 7 mole % $CaCl_2 \cdot 2H_2O$ in a thick glass tube to 360° C for 24 hours, the pressure reaching a maximum of 110 atmospheres. The sealed tube was then cooled in liquid nitrogen and cautiously opened to release the free chlorine. Then the product was washed with HCl and found to consist of 90% CrO_2. The possible reaction was thought to be:

$$CrO_3 + Cl_2 \longrightarrow CrO_2Cl_2 + \tfrac{1}{2} O_2$$

and then this CrO_2Cl_2 decomposes to give CrO_2. But Funke and Kleinert[48] found that the interaction with chlorine prevented the formation of pure CrO_2 and that by heating gradually and removing as much of the chlorine as possible gave pure CrO_2 at pressures above 60 Kg/mm^2.

Also, Demazeau et al[49] prepared a solid phase consisting entirely of CrO_2 by taking finely divided anhydrous or hydrated Cr_2O_3 in a gold tube subjected to an external pressure 2 Kb (2000 atmospheres) and a temperature of about 400° C for 45 to 120 minutes in the presence of the oxidising agent $HClO_4$. Several workers combined CrO_3 with dichromate.[50,51,52,53,54] Other oxides of chromium have also been used as starting materials. Amemiya et al[55] used a mixture of Cr_2O_5 and 0.1 μm diameter particles of CrO_2. Uchino et al[56] also used Cr_2O_5 which

was heated in a double vessel at 370° C and 124 Kg/cm^2 with sodium nitrate and water to form acicular particles of CrO_2.

Roger and Weisang[57] prepared CrO_2 particles by thermal decomposition of chromium tartrate, formate, or acetate which were heated in moist nitrogen at 250-300° C and then oxidised at a pressure of more than 90 Kg/cm^2 and a temperature above 360° C.

1.6.3 WITH ADDITIVES

Chromium dioxide particles for magnetic recording invariably have additives, the purpose of which is(1) to reduce the high temperatures and pressures involved in the decomposition of CrO_3 , (2) to encourage favourable growth habits in the particles (i.e. needle shape growth, grain size reduction), and (3) to modify the magnetic or other physical properties (i.e. Curie temperature, coercivity, abrasiveness). According to section 1.3.3 coercivity and retentivity depends on particle size. Particle size can be controlled by specific amount of modifier materials with the starting materials. Several workers modified the properties of CrO_2 by the addition of various metals and metallic oxides to get the desired results. Table 1.2 gives the effect of additives on morphology and magnetic properties.

Table 1.2

Sl.No.	Modifier	Wt %	Particle Size Length μm	Particle Size Width μm	Coercivity (H_c) Oe	Curie Temperature (T_c) °C	References
1.	Sb_2O_3	0 - 2	0.2 - 1.5	0.03 - 0.1	57 - 349	-	12,58
2.	Sb	0.29	0.2	0.025	440	-	59
3.	Te	0.2	1-3	0.5 - 1	increases	-	
		5	decreases	decreases	constant	-	40
		5	spherical particles		constant	-	
4.	Te + Ca	.25	0.2 - 0.5	0.01 - 0.1	470	-	60
5.	Te + Sn Te + Fe Sb + Fe	-	decreases	decreases	700	-	61
6.	Te + Sn + Fe	-	decreases	decreases	800	-	31
7.	$Ir(OH)_3$	2 5 10	decreases	decreases	640 850 1050	-	55
8.	W	1.5	decreases	decreases	540	reduces	62

(contd....)

Table 1.2 (contd.)

9.	1.1 % W						
	+ Ca	3			498		
	+ Zn	4			500		
	+ Mg	1.2	decreases	decreases	555	-	63,64
	+ Cu	1.5			570		
	+ Fe	-			600		
10.	Li, Na	small amounts	-	-	560	-	65
11.	Fluorine	-	-	-	-	reduces	66
12.	Sulphur	-	-	-	-	reduces very much	67
13.	Phosphorous	0 - 5	-	-	-	reduces	68
14.	Fe	0 - 3.9	-	-	-	116 - 154	69
15.	Fe	0.2	decreases	decreases	increases	-	70
16.	RuO_2	-	decreases	decreases	increases	-	71
17.	RhO_2	.0001-.01	-	-	180-370	-	72
18.	Fe, Ir, Ru	-	-	-	-	increases by 19,4,2 from 128 respecti vely	70
	V,As,Sb,Re, Mo,W	2%	-	-	-	reduces by 20,21,10,37, 38,42 from 128 respectively	

On the basis of the effect of different additives on coercivity of CrO_2 , Kubota[40] found that

(1) Those did not reduce the grain size at all, (Fe, Co, Ni and V)

(2) Those that reduce the grain size slightly (Cd, Ag, Al, B, Zn, alkaline metals)

(3) Those that reduce the grain size considerably and the grains become acicular (Pt, Sb, Ru, Te) .

But Shannon et al[70] found that addition of Fe^{3+} ions in excess of 0.2 wt% reduces the particle size and thereby increases the coercivity.

Also MnO_2[73] and VO_2[74] form solid solutions with CrO_2 and thereby reduce both the specific magnetization and the Curie temperature and this was explained by the decrease in the exchange force among Cr^{4+} ions.

1.7 STRUCTURE AND PROPERTIES OF CrO_2 PARTICLES

1.7.1 STRUCTURE

The formula CrO_2 was established by Michel and Benard who also found that the compound had the rutile structure. It was confirmed by Wilhelmi and Jonsson[75] and found the tetragonal structure with a_o = 4.423 Å ; C_o = 2.917 Å and the density = 4.83 gm/cc. Later on many workers confirmed the above result as shown in Table 1.3.

Table 1.3

'a' Å	'c' Å	References
4.423	2.917	75
4.421	2.916	42
4.41 $\pm$ 0.01	2.91 $\pm$ 0.01	12
4.4218	2.9182	14
4.420	2.916	77
4.421	2.916	47
4.424	2.918	78
4.4289	2.9175	70
4.410	2.860	79
4.4190	2.9154	80

The space group of CrO_2 is D_{4H}^{14} - $P4_2$ / mnm (ASTM). The chromium ions are situated at the corners as shown in Fig. 1.5 and the body of the tetragonal unit cell giving two chromium ions per unit cell. The oxygen ions are found at (u, u, 0), ($\bar{u}$, $\bar{u}$, 0), (u - $\frac{1}{2}$, $\frac{1}{2}$ - u, $\frac{1}{2}$), and ($\frac{1}{2}$ - u, u - $\frac{1}{2}$, $\frac{1}{2}$) where the value of u was determined by Siratori and Iida[76] for diffraction measurements as 0.294 and by Cloud et al[14] as 0.301 ± 0.04. Hirota et al[67] found that addition of sulphur up to 0.17 wt % increases 'a' and 'c' does not change. Chamberland et al[66] found that addition of fluorine upto 0.3 wt % increases the value of 'a' and 'c'. Sirotari and Iida[76] first observed and Darnell and Cloud[15] confirmed that the lattice constant 'c' decreasing with increasing temperature.

1.7.2 PHYSICAL AND THERMAL PROPERTIES

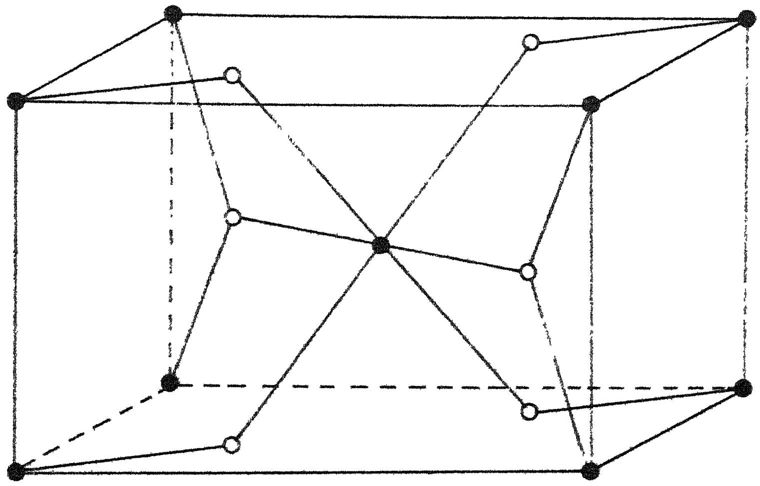
Colour - brown black powder

Solvent - Concentrated HNO_3

Density - 4.89 gm/cc

Melting point - At 300° C, it looses oxygen.

State	ΔH_f° (KCal/mole)	ΔG_f° (KCal/mole)	S°(at 25°C) (Cal/deg/mole)	C_p (Cal/deg/mole)
Gaseous	- 18.00	- 20.88	64.32	10.32



● = Cr^{4+}
○ = O^{2-}

Fig. 1.5. Structure of CrO_2

1.7.3 MAGNETIC AND ELECTRICAL PROPERTIES

The formula CrO_2 suggests that the chromium ions are in the Cr^{4+} states for which a magnetic moment per ion of 2β is expected. Therefore, since the material is ferromagnetic rather than ferrimagnetic the saturation magnetization per unit mass can be calculated from $\sigma_s = (n_\beta \cdot 5587)/M$, where M is the molecular weight, 84.01 for CrO_2. Using $n_\beta = 2$, σ_s was calculated as 133 emu/gm. This value was indeed obtained by several investigators:

σ_{s0} emu/gm (0°K)	σ_s (20°C) emu/gm	n_β	References
138.3	-	2.07 ± .03	81
137.3 ± .02	-	2.01 ± .03	41
100 ± 1	100 ± 1	-	12
-	-	1.96	47
-	-	2.00 ± 0.5	15

Also Darnell and Cloud[15] found that CrO_2 is difficult to saturate with the difficulty increasing with decreasing particle size. In the fields of 10000 Oe, which are much

greater than the anisotropy fields, the magnetization reached only 94 to 98% of saturation. The effect was attributed to the lower symmetry experienced by surface chromium atoms, resulting in larger and randomly directed anisotropies. The conclusion was confirmed when measurements on single crystals in the same field gave results closer to saturation by Swoboda et al.[12] Demagnetization factor σ_r/σ_s greater than 0.9 can be obtained for CrO_2 .

A certain additives like Fe, S, F also affects the intrinsic magnetic properties like specific magnetization and Curie temperature. Additives like Sb_2O_3 , Te, Ir reduces the particle size and hence increased the coercivity (Refer Table 1.2).

CrO_2 shows room temperature resistivity of 2.5×10^{-4} Ω cm and hence it has metallic conductivity at room temperature. Between -193° C and 302° C it shows positive temperature coefficient.

1.7.4 AIM AND STATEMENT OF THE PROBLEM

The aim of the present work is to prepare CrO_2 by a low cost method and characterize it along the lines envisaged in chapter I so that it could be exploited for magnetic tape materials. From the work referred to in

chapter I, it is clear that most of the investigators have prepared CrO_2 under high pressures. Use of high pressures and high temperatures involve high cost. So if CrO_2 could be prepared at atmospheric pressure, it would clearly be an advantage and, more over, the cost of production can be reduced sustantially. Such methods have been described in literature. Fukuda[33], for example, developed a rather simple method to prepare CrO_2 for tape applications. In this method CrO_3 and KNO_3 were dissolved in water. After drying, the residue was heated to 415° C for 45 minutes to get CrO_2 . This method has been chosen for the present study with and without additives like Sb_2O_3 , Fe, Co, Ni. The effect of additives on the phase composition, yield morphology, and magnetic properties of CrO_2 have been investigated. The phase composition was established by X-ray analysis. DTA, TG analysis was used to find out the yield of CrO_2.

Correlations between particle size and shape and magnetic properties have been studied and these have been compared with the properties of CrO_2 provided by one of my guides, Dr. P. Raghunathan.

CHAPTER II

EXPERIMENTAL PROCEDURES

2.1 PREPARATION

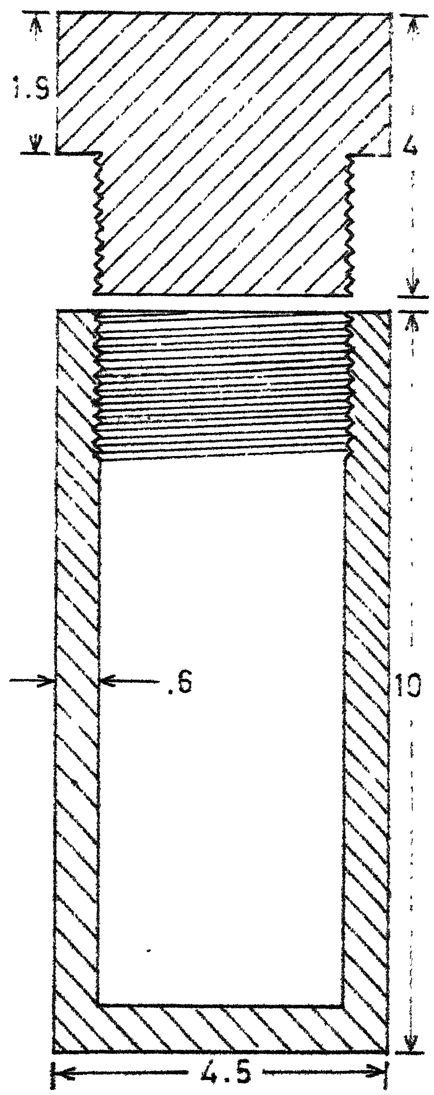
We have used a method developed by Fukuda[33] which seems to be most simple and low cost method of all the methods described in chapter I for studying the fundamental properties of CrO_2 leading to magnetic tape applications.

2.1.1 APPARATUS

A mild steel rod is machined as shown in Fig. 2.1 to serve as a tubular container for the preparation of CrO_2 . This mild steel container is charged with the starting materials and heated in a resistance heated furnace with constant temperature profile which could go well beyond the reaction temperature i.e. 415° C. The temperature of the system is measured with a Chromel- Alumel thermocouple and the temperature of the furnace is controlled by an 'Aplab' Model No.: 9601 temperature controller within ± 1° C.

2.1.2 STARTING MATERIALS

The starting material is CrO_3 containing 0.1% of sulphate and chloride ions and of absorbed water as major impurities. Potassium nitrate is added to decompose CrO_3



Dimensions are in cm.

Fig. 2.1

at atmospheric pressure to give CrO_2. Antimony sequoxide (Sb_2O_3), anhydrous ferric chloride ($FeCl_3$), Cobaltous chloride ($CoCl_2 .6H_2O$), and Nickel chloride ($NiCl_2.6H_2O$) are added to CrO_3 and KNO_3 to control the particle size and shape and thereby improve the magnetic properties of chromium dioxide.

2.1.3 PROCEDURE

First chromium trioxide (CrO_3) and potassium nitrate are weighed and dissolved in distilled water. The additives like $FeCl_3$, $CoCl_2 .6H_2O$, and $NiCl_2.6H_2O$ are weighed separately and dissolved in the solution containing CrO_3 and KNO_3 separately to give different batch composition. Antimony sequoxide (Sb_2O_3) does not dissolve in water. Therefore it is weighed separately and added to the batch before putting the container into the furnace. The batch composition for different samples is given below:

Sample NO:TR 1

CrO_3 = 18 gms (90%)

KNO_3 = 2 gms (10%)

Sample NO:TR 2

CrO_3 = 17 gms (85%)

KNO_3 = 2.8 gms (14%)

Sb_2O_3 = 0.2 gms (1%)

Sample NO: TR 3

CrO_3 = 17 gms (85%)

KNO_3 = 1.8725 gms (9.3625%)

Sb_2O_3 = 0.1275 gms (0.6375%)

$FeCl_3$ = 1 gm (5%)

Sample NO: TR 4

CrO_3 = 17 gms (85%)

KNO_3 = 1.8725 gms (9.3625%)

Sb_2O_3 = 0.1275 gms (0.6375%)

$CoCl_2 .6H_2O$ = 1 gm (5%)

Sample NO: TR 5

CrO_3 = 17 gms (85%)

KNO_3 = 1.8725 gms (9.3625%)

Sb_2O_3 = 0.1275 gms (0.6375%)

$NiCl_2.6H_2O$ = 1 gm (5%)

Then the solution containing mixture of starting materials and additives is heated at a slow rate so that the water will evaporate to give a black mass of the batch. This dried mass is then transferred to the mild steel container and Sb_2O_3 is added. The container is closed with a mild steel cap and put inside the furnace.

The furnace is next heated at a slow rate to 415°C at which temperature it is maintained for 45 minutes. After cooling the system, the container is opened, and a black mass containing CrO_2 could be seen inside. This material is recovered carefully and ground in a mortar to give a fine powder. The fine powder is then washed with acetone and dried. Now the product is ready for further study.

The sample (A1) provided by Dr. P. Raghunathan was prepared by the method developed by Funke et al.[48] The reaction is as follows:

$$CrO_2Cl_2 + O_2 \xrightarrow[60\ \text{atm.pr.}]{380-400^{\circ}C} CrO_2 \quad \text{(very pure).}$$

2.2 CHARACTERIZATION

2.2.1 X-RAY ANALYSIS

The X-ray diffraction pattern of the sample in the form of fine powder, is obtained with the help of GE-XRD-6 Diffractometer. Cu(K_α) radiation of wavelength 1.5405 Å with Ni filter at 500 cps and at a scanning speed of 2° per minute is used for getting the powder pattern of CrO_2. The dry fine power of CrO_2 could stay with difficulty in the cavity of the sample holder. Hence 2 to 3 drops of acetone is added to the powder to moisture it a bit.

2.2.2 ELECTRON MICROSCOPIC STUDY

Here 'Philips' Transmission Electron Microscope Model 301G is used to analyse the samples. To prepare the specimen for electron microscopic study, a pinch of CrO_2 is put into some supporting liquid, acetone, in a 50 ml beaker which is then kept in the water tank of an ultrosonic generator. Five minutes of operation of the ultrasonic shaker dispersed the particles sufficiently. Now one drop of this acetone in which CrO_2 particles have already been dispersed is put on a carbon coated grid which is kept on a blotting paper. Now a small glass trough containing distilled water is set ready over which a drop of collodion liquid is put. The collodion forms a film on the surface of the water. Care is taken to prevent any disturbance on the surface of the water because this will squeeze the collodion film formed. Then the carbon coated grid containing the specimen is taken with the help of a tweezer and put on the collodion film. Now a clean glass slide is brought vertically and pushed down past the surface. The film folds back against the surface. Finally, the slide is turned and lifted out of water and the excess water is blotted off. Now the grid may be lifted free of the slide after drying, which are now ready to yield electron micrographs.

2.2.3 DIFFERENTIAL THERMAL ANALYSIS (DTA), THERMOGRAVIMETRY (TG) AND DERIVATIVE THERMOGRAVIMETRY (DTG)

D.T.A., T.G. and D.T.G. are important experimental techniques to obtain information about specific chemical and physical transformations that are accompanied by evolution or absorption of heat or by change in weight. Here MOM (Hungery) Derivatograph is used to find out the weight loss and characteristic temperature of the transformation $CrO_2 \rightarrow Cr_2O_3$. From the weight loss data, the percentage of chromium dioxide present in the sample can also be calculated.

2.2.4 MAGNETIC MEASUREMENTS

Magnetic measurements are done with Princeton Applied Research Vibration Sample Magneto meter (VSM). Coercivity (H_c) saturation magnetization (σ_s), Remanence magnetization and hence a value of squareness ($S = \frac{\sigma_r}{\sigma_s}$) are measured. Curie temperatures is measured at 2000 oersteds. Samples for this magnetic measurements are prepared in a glass ampoule. Glass ampoules of height less than 5 mm and outerdiameter less than 3 mm with one side closed are prepared to suit the sample holder of the VSM. The weight of the empty ampoule is measured with a high- accuracy one pan balance. The sample CrO_2 is then

packed well inside the ampoule. Then the total weight of the material plus ampoule is taken. From this, the sample weight is calculated. After this, the ampoule containing the sample is taken out carefully from the balance and the open end is sealed with Araldite so that no material streams out when the high magnetic field of 10,000 Oe or so is switched on. Now the sample is ready for magnetic measurements.

CHAPTER III

RESULTS AND DISCUSSION

3.1 X-RAY ANALYSIS

To determine the various phases present in the product and the lattice parameters of CrO_2 (known to have a tetragonal structure), an X-ray analysis was carried out. In Table 3.1, observed diffraction data for different CrO_2 samples with and without additives are given. In the table, d_{obs} is the interplanar spacing observed and d_{calc} is the interplanar spacing calculated using the following formula for the tetragonal system:

$$\frac{1}{d^2} = (h^2 + k^2)/a^2 + l^2/c^2$$

For obtaining d_{calc} , the values of 'a' and 'c' were calculated from 2θ for 310 and 002 planes respectively and are given in Table 3.1. These are in good agreement with the results obtained by other investigators, as shown in Table 1.3. The variation in additives such as Sb_2O_3 , $FeCl_3$ (anhydrous), $CoCl_2.6H_2O$, and $NiCl_2.6H_2O$ contents did not show any shift in the peaks of different 2θ values. This means that the solubility of the abovementioned additives in CrO_2 is almost negligible. Moreover, the X-ray diffraction patterns for these samples show that there will

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Table 3.1

Sample No	'a' Å	'c' Å
A1	4.419	2.911
TR1	4.413	2.928
TR2	4.421	2.914
TR3	4.413	2.907
TR4	4.425	2.915
TR5	4.419	2.919

be a Cr_2O_3 phase other than CrO_2 . But X-ray intensities for CrO_2 and Cr_2O_3 phases reveal that the major phase is CrO_2.

As discussed in chapter I, it is now well established that decomposition of CrO_3 at atmospheric pressure and at high temperature (415° C) results in CrO_2 alongwith Cr_2O_3 . It is due to the fact that eventhough addition of potassium nitrate controls the decomposition of CrO_3 to result in CrO_2 , the high temperature and atmospheric pressure favour the formation of Cr_2O_3 .

3.2 YIELD

The percent yield of CrO_2 is calculated according to the equation:

$$\underset{(100)}{CrO_3} \longrightarrow \underset{(84)}{CrO_2} + \tfrac{1}{2}\, O_2$$

According to which if 100 gm of CrO_3 is taken and 84 gms of CrO_2 is produced, the yield will be 100%. However, when the product is taken out from the container some of the CrO_2 will be lost and while grinding also some of the CrO_2 will be lost. In addition to this, washing of CrO_2 to remove undesirable compounds may result in some loss. These are the two inevitable possibilities of losses. Here

we are not taking into account these losses.

According to the last section, because of the presence of Cr_2O_3 phase, the yield will be some what lower than what we could expect. Here the yield calculation is based on Kubota's[42] work. When pure CrO_2 is heated in air, at its characteristic temperature, it will be transformed to Cr_2O_3 phase. This is shown in the following equation:

$$\begin{array}{ccc} 4\,CrO_2 & = & 2\,Cr_2O_3 + O_2 \\ (336) & & (304) \quad (32) \end{array}$$

D.T.A. and T.G. analysis[82] showed that around $550^{o}C$ CrO_2 was indeed transformed into Cr_2O_3 phase. During this transformation, CrO_2 showed a weight loss. This weight loss can be calculated as follows:

336 gms of CrO_2 transformed to 304 gms of Cr_2O_3

So the remaining 32 gms of oxygen is accounted for the weight loss since it is released during the transformation. If a sample consists of CrO_2 and Cr_2O_3 phase, Cr_2O_3 would not show any weight loss since it is a very stable phase at high temperatures. So the weight loss is mainly due to the transformation of CrO_2 only. From this we can easily calculate the amount of CrO_2 present in the total

weight of the sample. For example, the total weight ($CrO_2 + Cr_2O_3$) of the sample is 100 gms and the weight loss is 4 gms , according to the above equation,

If 32 gms of oxygen is released, there is 336 gms of CrO_2 present.

So if, 4 gms of oxygen is released, there is $\frac{336}{32}$ X 4 gms of CrO_2 present.

= 42 gms of CrO_2

So in the total weight of the sample, the amount of CrO_2 present is 42 gms only. So the yield is 42%. Likewise, the yields for all the samples are calculated.

3.2.1 EFFECT OF ADDITIVES

Table 3.2 gives the total weight of the samples taken, weight loss accounted, and the percentage of CrO_2 present in these samples or yield of CrO_2. These are calculated from the D.T.A., T.G. and D.T.G. curves which are shown in Fig. 3.1 to 3.6.

Table 3.2

Sample No	Total weight of the samples (mg)	weight loss (mg)	% yield of CrO_2
A1	250	20	84
TR1	1191	33	29.1
TR2	900	40	46.7
TR3	680	25	38.6
TR4	473	39	86.6
TR5	900	38	44.3

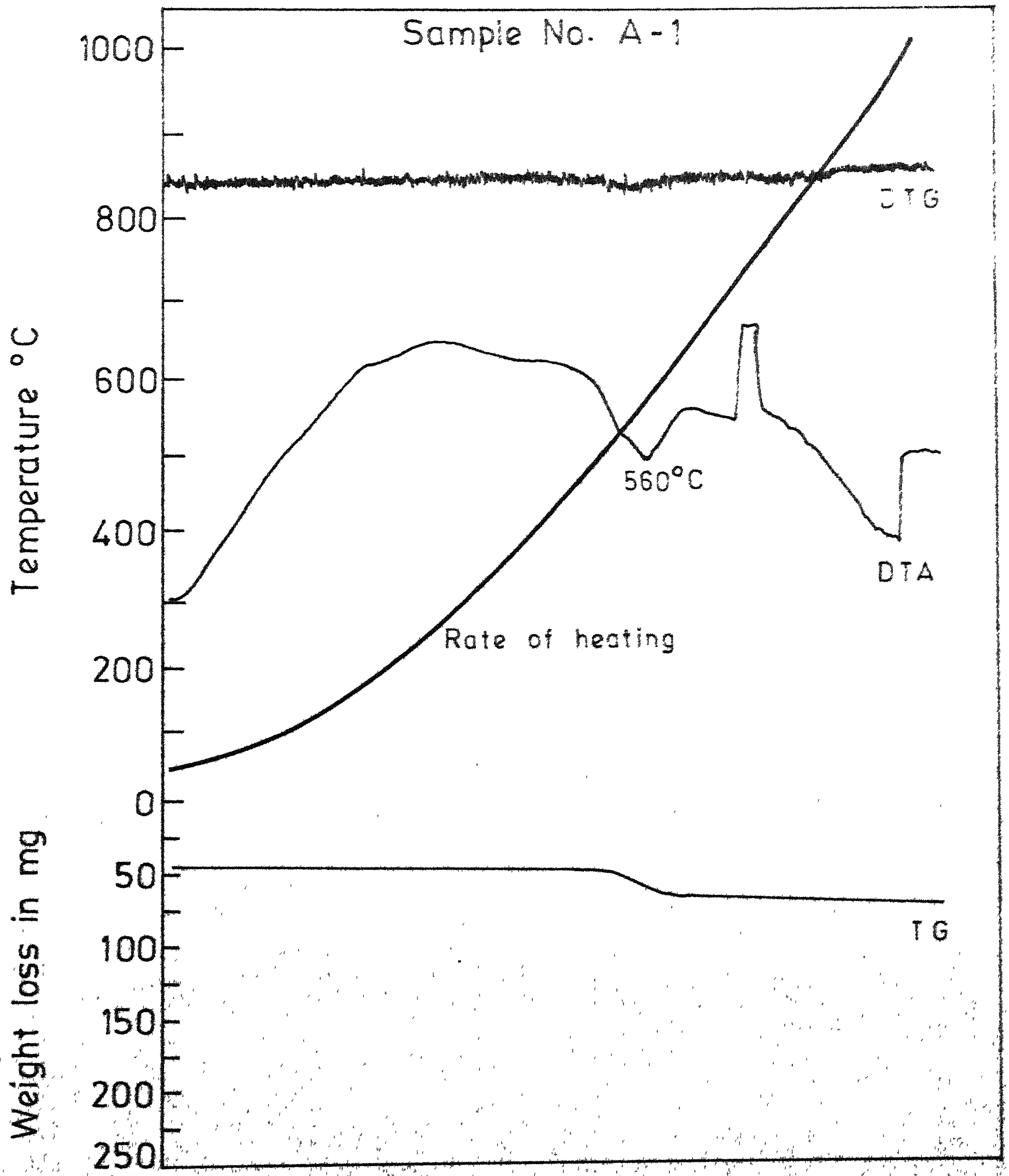
Sample No. A-1
1000
800
600
400
200
0
50
100
150
200
250
Temperature °C
Weight loss in mg
DTG
560°C
DTA
Rate of heating
TG

Fig. 3.1

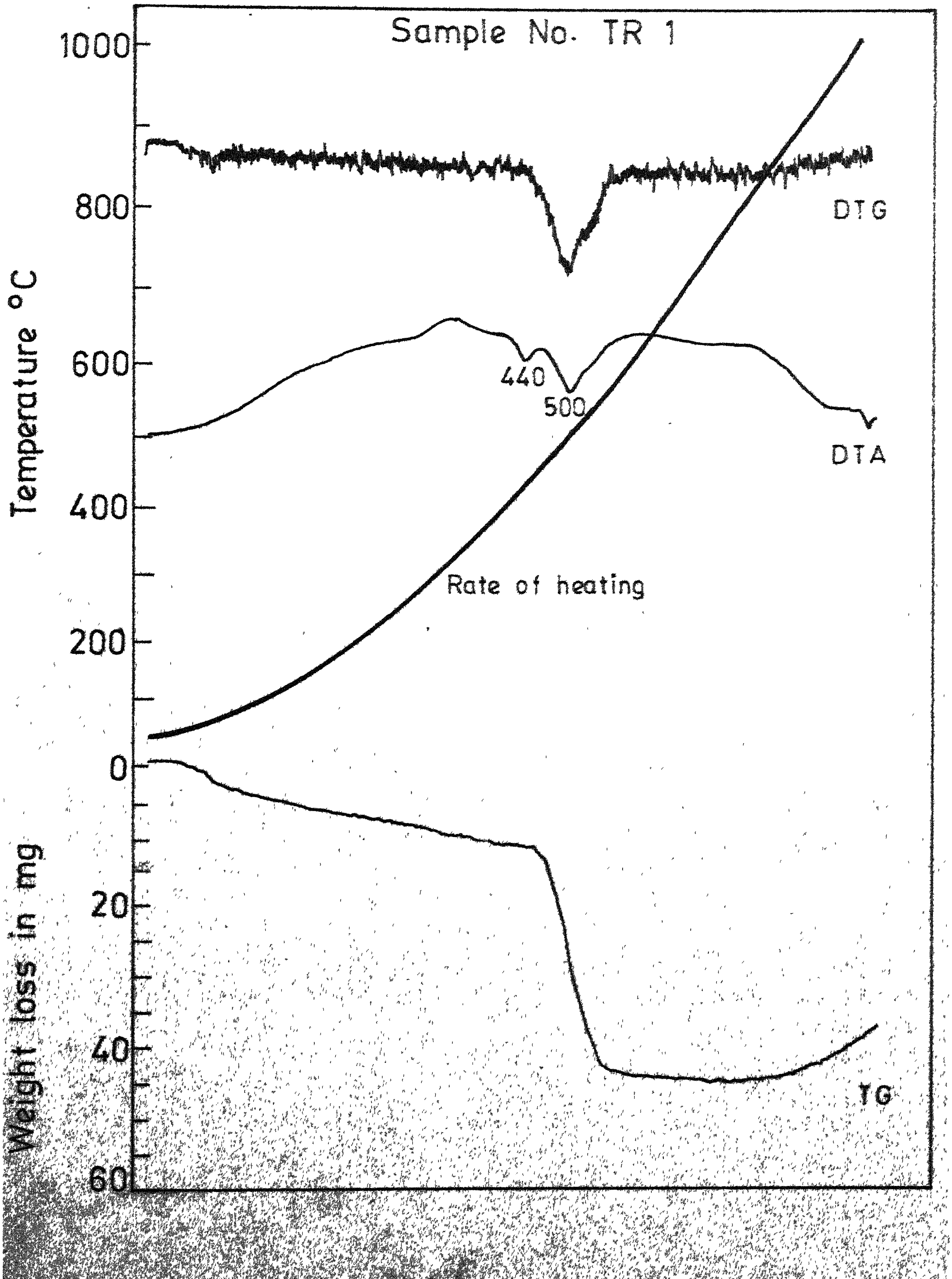
Sample No. TR 1
1000
800
600
400
200
0
20
40
60
Temperature °C
Weight loss in mg
DTG
440
500
DTA
Rate of heating
TG

Fig. 3.2

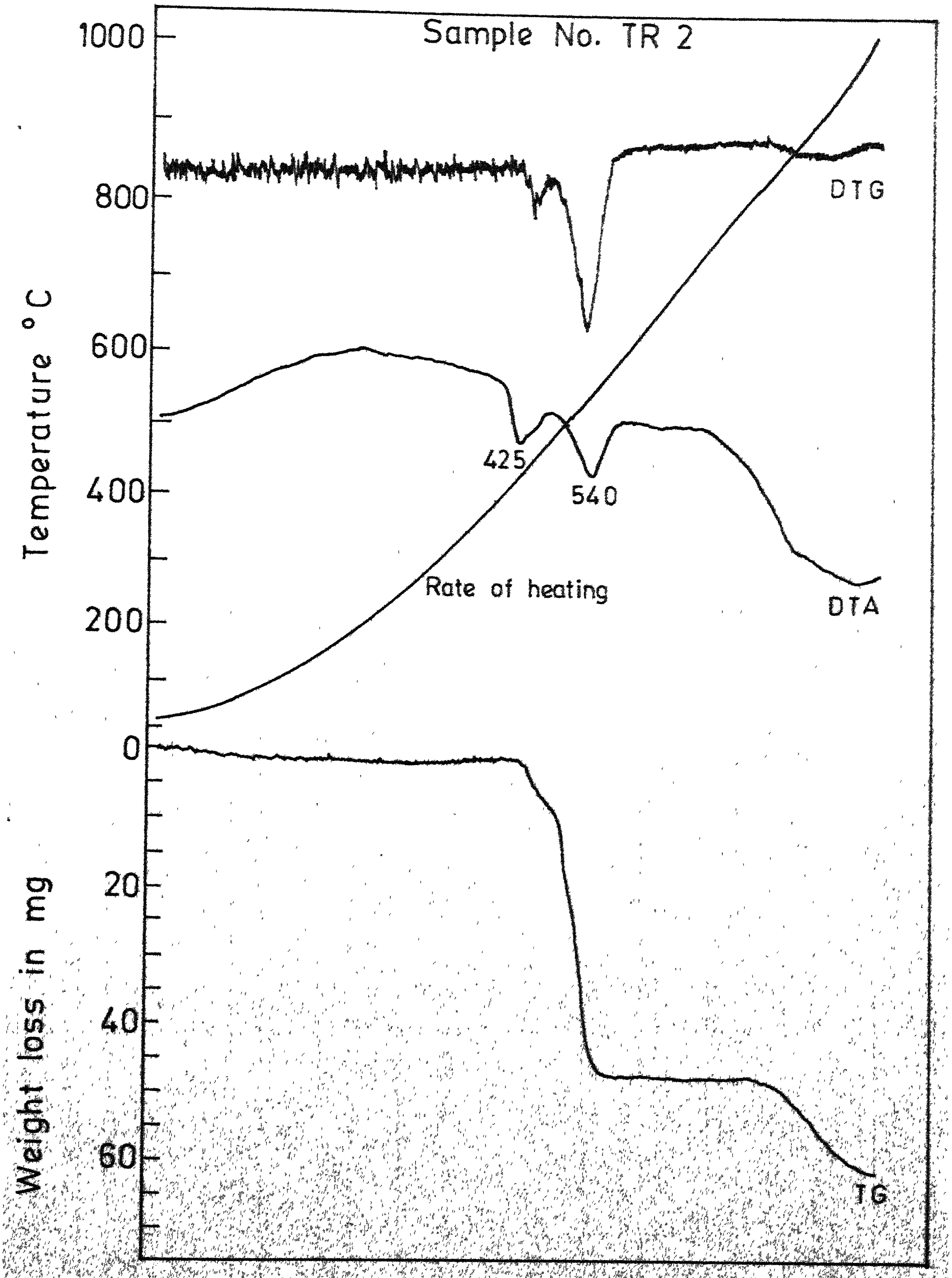
Sample No. TR 2
1000
800
600
400
200
0
Temperature °C
DTG
425
540
Rate of heating
DTA
20
40
60
Weight loss in mg
TG

Fig. 3.3

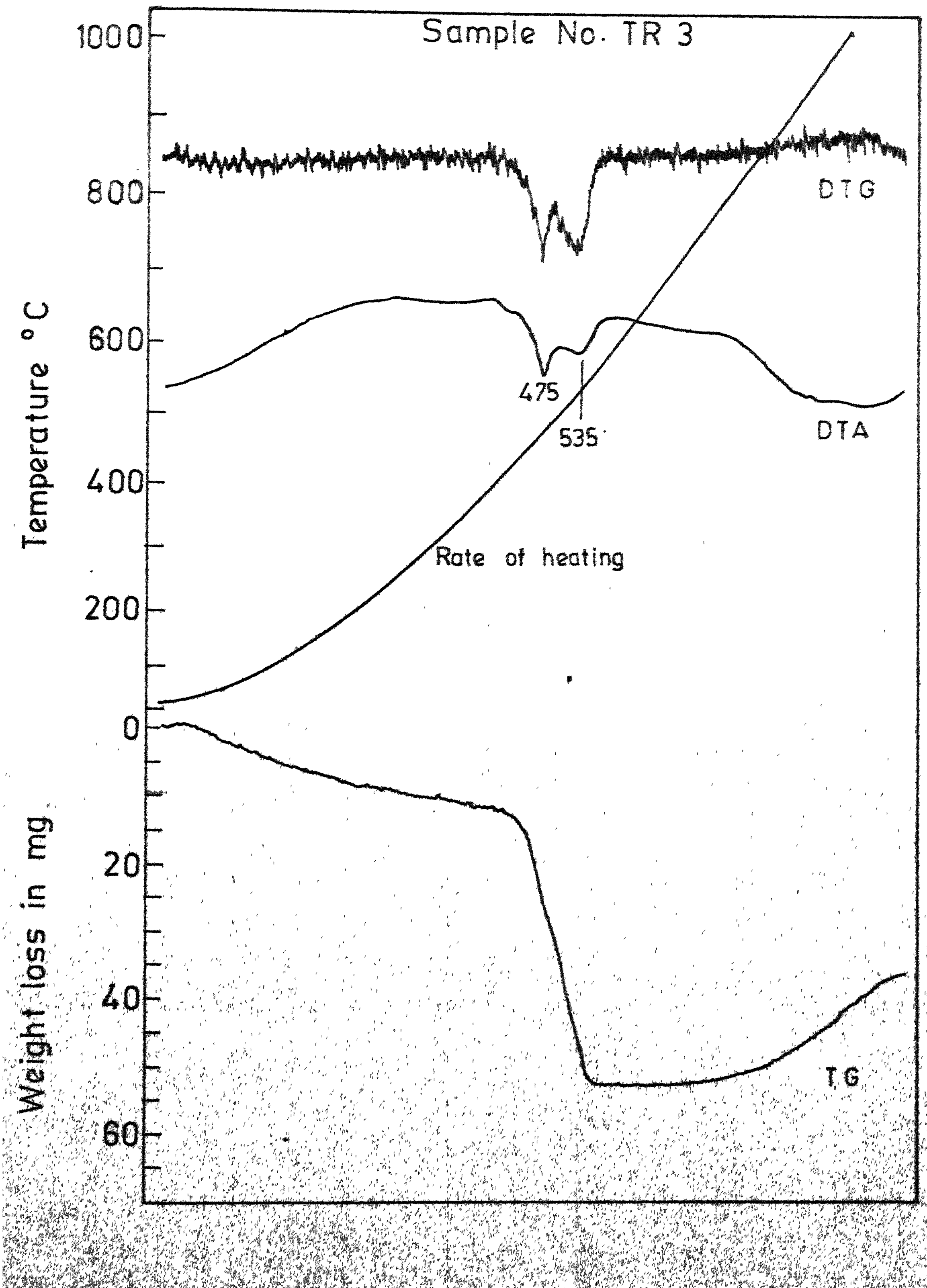
Sample No. TR 3
1000
800
600
400
200
0
20
40
60
Temperature °C
Weight loss in mg
DTG
DTA
475
535
Rate of heating
TG

Fig. 3.4

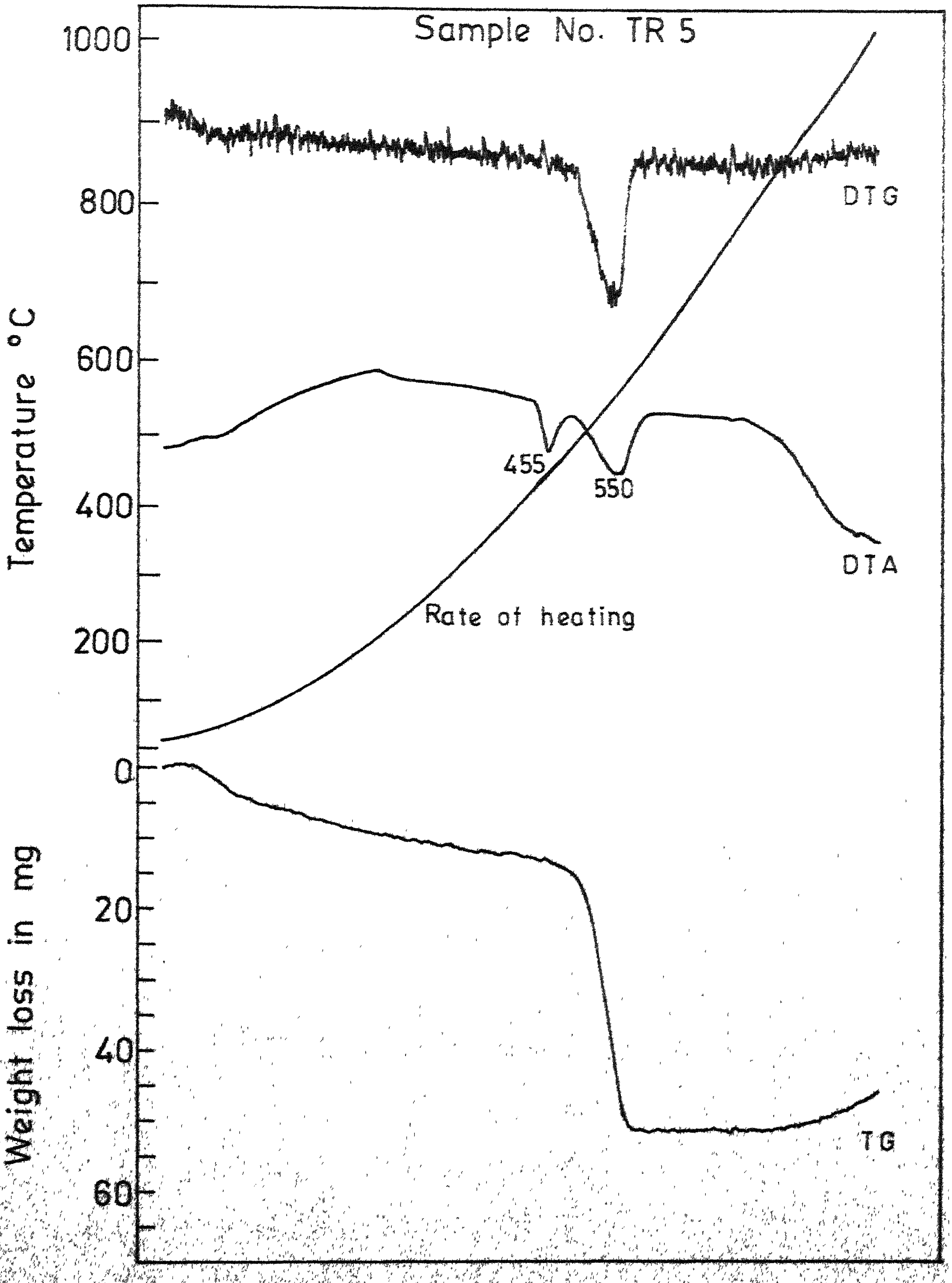
Sample No. TR 5
1000
800
600
400
200
0
20
40
60
Temperature °C
Weight loss in mg
DTG
455
550
DTA
Rate of heating
TG

Fig. 3.6

From the Table 3.2, it is known that for pure CrO_2 (A1) the yield is 84%. Because of the presence of Cr_2O_3 phase, the yield for other samples varying substantially. Also it is seen that the presence of additives increased the yield. Without additive, the sample TR1 showed 29.1% yield. The addition of .1% Sb_2O_3 (TR2) increased the yield to 46.7%, 5% Fe (TR3) increased the yield to 38.6% and 5% Ni (TR5) increased the yield to 44.3%. It is noteworthy to see that 5% Co (TR4) increased the yield to 86% . So we conclude that the presence of Cobalt ion in CrO_2 prevents the formation of Cr_2O_3 phase.

Also it is seen from the D.T.A. curves of Fig. 3.1 to 3.6, around 440^{o} C, another transformation is taking place. From the behaviour of oxides in chromium chemistry, the following high- temperature oxidation reactions are likely to have occured in our reaction mixture especially in the presence of KNO_3. When KNO_3 is heated, which decomposes into potassium monoxide and which in turn reacts with CrO_3 to form potassium chromate. The next reaction is that the formation of potassium dichromate from potassium chromate and CrO_3. Small amounts of this salts present in the samples will be sufficient to explain the additional peaks in D.T.A. curves.

3.3 MORPHOLOGY

Some typical electronmicrographs are given in plates 1 to 8. A general view of these electro micrographs suggests that a fairly good number of samples has needle like shape, which we are interested in, though the size is not uniform. In some samples the particles are having mixed shape i.e. rods, acicular, platelets (refer to plate 4). The cause of this variation may be due to the presence of additives such as Sb_2O_3, Fe, Co, Ni. The electronmicrograph of the sample A1 shows that CrO_2 particles are present having clean acicular shape free of dentrites. Also the micrographs of the samples TR1 - TR5 (4 to 8) show CrO_2 particles having acicular shape as well as small particles belonging to another phase. Our X-ray analysis has showed that CrO_2 is present along with Cr_2O_3 . Also Kubota[42] found from his electronmicrographs that Cr_2O_3 particles are of small size and when CrO_2 is converted into Cr_2O_3 , the straight edges of large grains of CrO_2 are broken first and split into small particles of Cr_2O_3. We therefore, conclude that the other phase is Cr_2O_3 and X-ray analysis also supports this conclusion.

For magnetic tape application, one is interested in only acicular particles of uniform size so that the

MORPHOLOGY OF CrO_2 PARTICLES

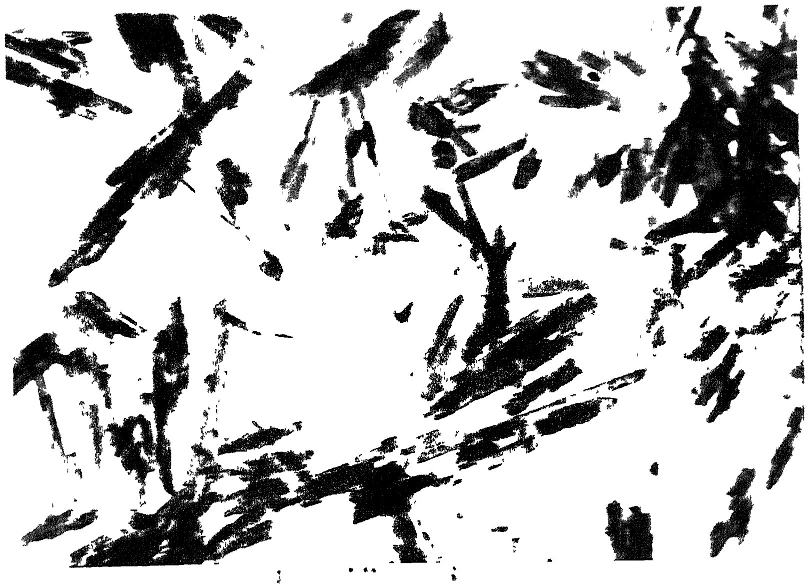

Plate No. 1 (A1) (6300X)

Plate No. 2 (A1) (10000X)

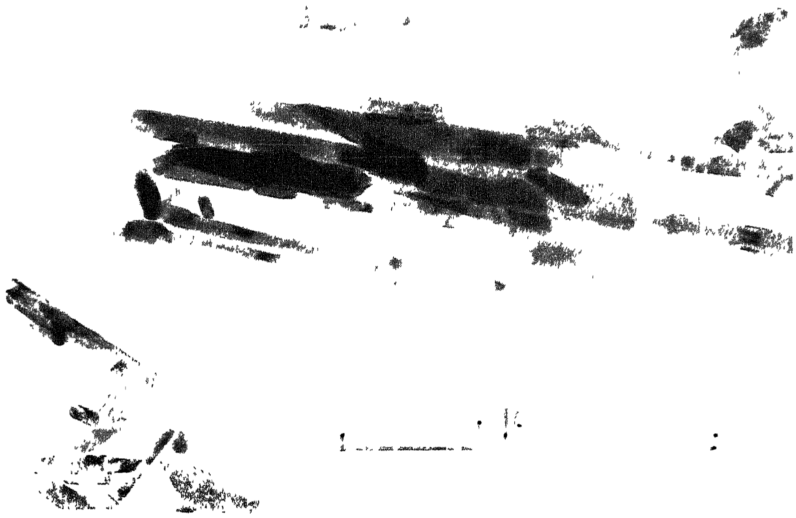

Plate No.3 (A1) (13000X)

Plate No.4 (TR1) (2200X)

EFFECT OF ADDITIVES ON MORPHOLOGY OF CrO_2 PARTICLES

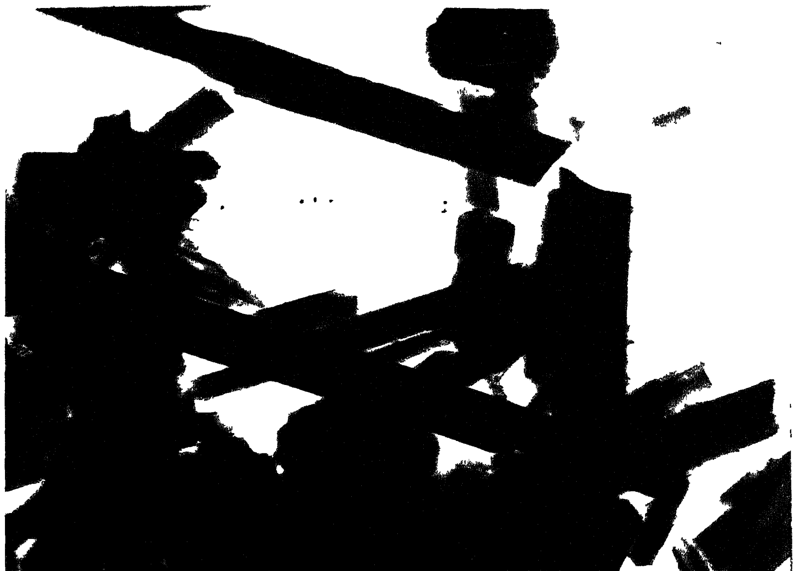

Plate No.5 (TR2) (7800X)

Plate No.6 (TR3) (7800X)

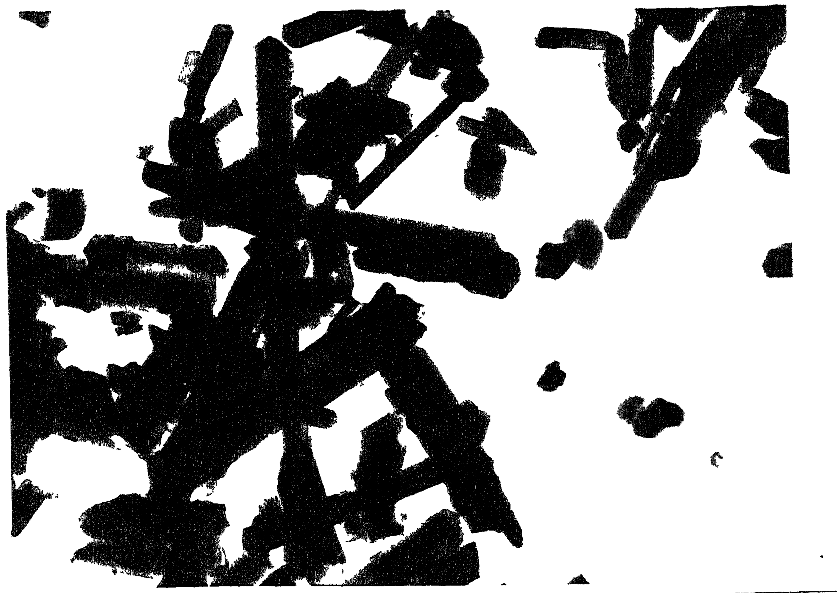

Plate No.7 (TR4) (5400X)

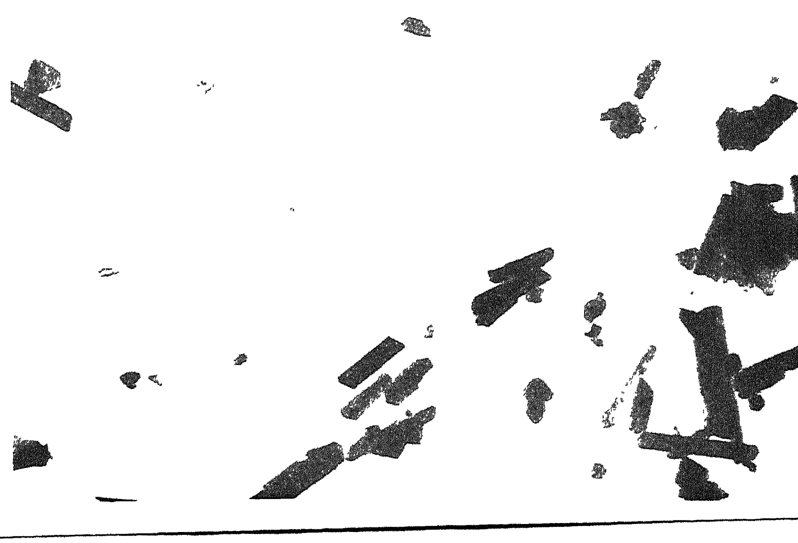

Plate No.8 (TR5) (2800X)

the spread in coercivity and retentivity may not be too large. Hence this property is very important to reckon with.

The particle size was determined by taking the average of about five particles located at different parts of an electronmicrograph. The effect of additives such as Sb_2O_3, Fe, Co, Ni on morphology has been investigated.

3.3.1 EFFECT OF ADDITIVES

Table 3.3 gives the effect of additives on the particle size of different samples.

Table 3.3

Sample No.	Plate No.	Average Particle Size		L/W
		Length (μ)	Width (μ)	
A1	1,2,3	0.5	0.05	10
TR1	4	2	0.5	4
TR2	5	1.7	0.22	7.7
TR3	6	1.5	0.24	6.3
TR4	7	1.5	0.2	7.5
TR5	8	1.1	0.25	4.4

From the above Table we know that the sample A1 has particle size smaller than other samples. Also (c.f. plates 1,2,3) this shows clear acicularity of CrO_2 particles. Sample TR1 (plate 4) shows that the particle size is larger than other samples and contained Cr_2O_3 phase. But addition of 1% Sb_2O_3 (TR2) (plate 5) reduces the particle size considerably (from dimensions 2 μ x 0.5 μ to 1.7 μ x 0.22 μ). But addition of Fe, Co, Ni (TR3, TR4, TR5) (plate 6,7,8, respectively) reduce the particle size very slightly. The reduction of particle size is well correlated with the increase of coercivity, and the values of H_c for this samples are reported in the next section. If the particle size approaches the single domain size and free of any other impurity phase, the coercivity increases with respect to decrease in particle size. So, for the sample A1 (pure CrO_2) coercivity is high because its particle size is smaller than other samples. Also, the increase of coercivity can be seen in other samples (TR2, TR3, TR4, TR5) having smaller particle size than the sample TR1. However, the coercivities for these samples are less than for the sample A1 because they all contain the Cr_2O_3 phase which affects magnetic properties.

3.4 MAGNETIC PROPERTIES

Table 3.4 shows coercivity (H_c), saturation magnetization (σ_s) remanence magnetization (σ_r) and σ_r / σ_s and Fig. 3.7 to 3.10 shows the plot of magnetic moments per gram versus temperature at 2000 Oe.

Table 3.4

Sample No.	H_c Oe	σ_s emu gm^{-1}	σ_r emu gm^{-1}	σ_r / σ_s
A1	340	82.2	29.1	0.3546
TR1	80	16.9	3.3	0.1956
TR2	90	38.0	9.0	0.2368
TR3	160	37.8	7.8	0.2059
TR4	140	72.2	15.3	0.2115
TR5	100	46.2	5.8	0.1250

3.4.1 EFFECT OF ADDITIVES

From this Table, we know that the sample No. A1 (pure CrO_2) gives comparatively superior magnetic properties than other samples. This is due to the fact that other samples contain a fair amount of Cr_2O_3 phase. Also, addition

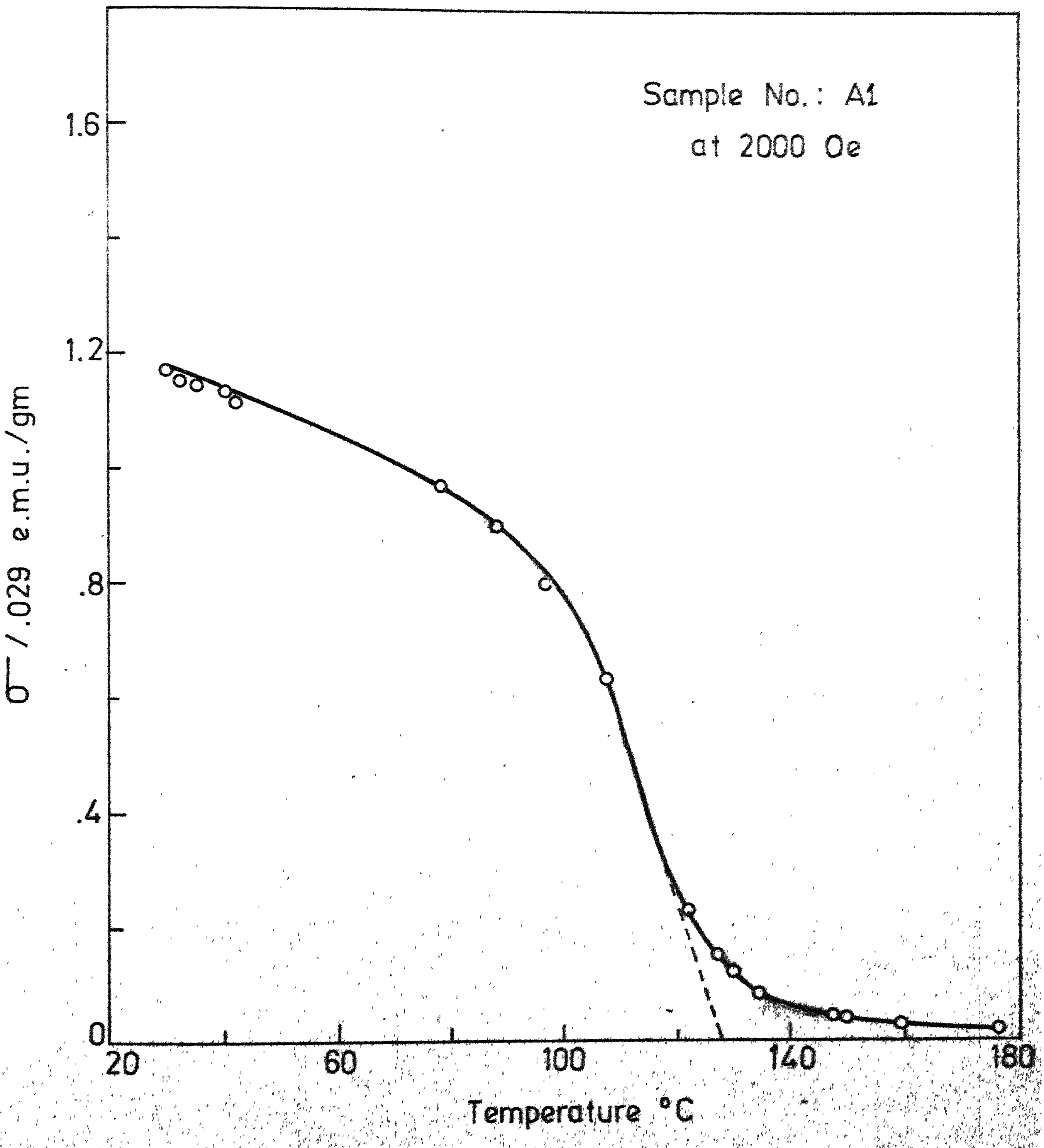
Sample No.: A1
at 2000 Oe
1.6
1.2
.8
.4
0
σ /.029 e.m.u./gm
20
60
100
140
180
Temperature °C

Fig. 3.7

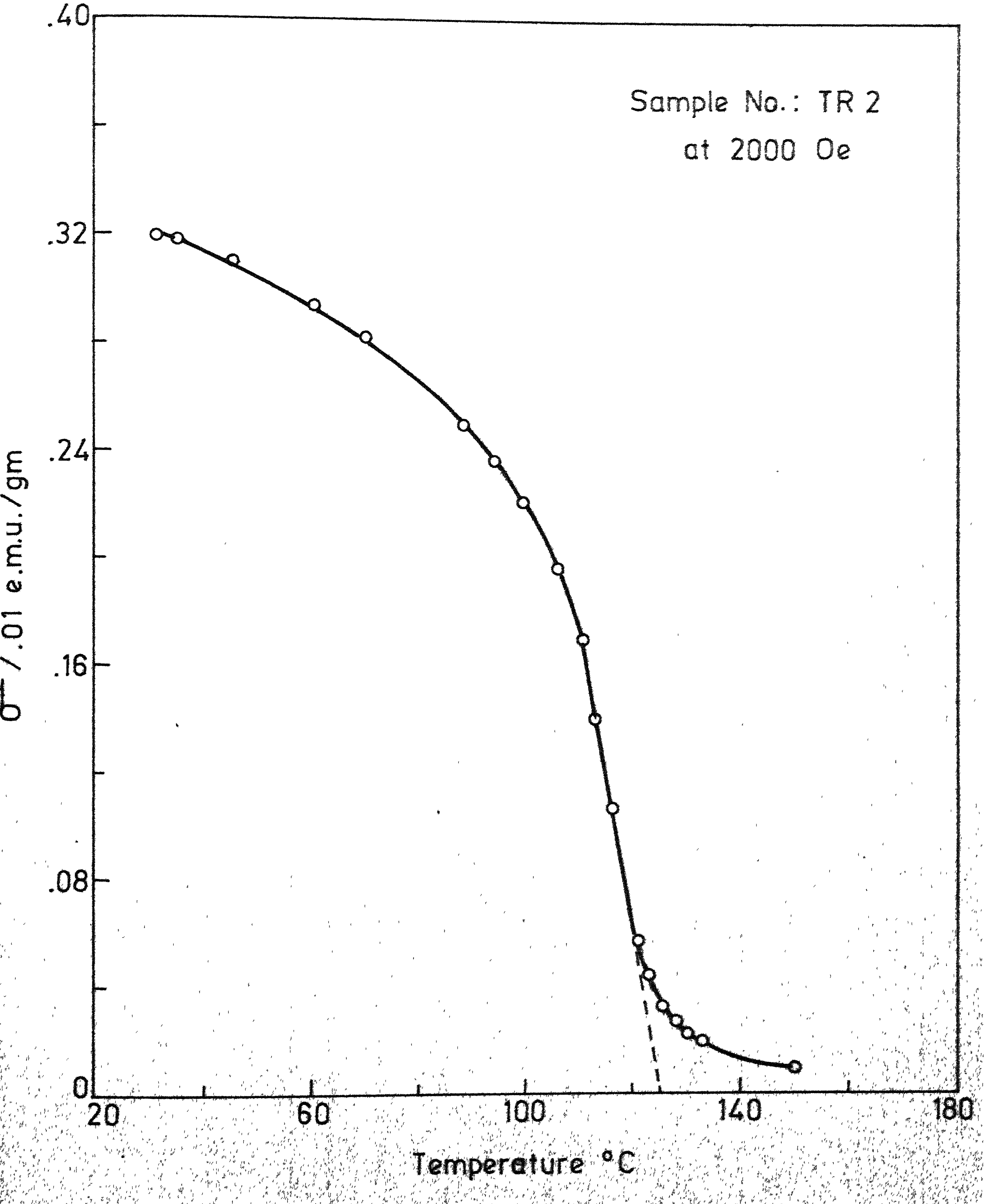
Sample No.: TR 2
at 2000 Oe
.40
.32
.24
.16
.08
0
σ /.01 e.m.u./gm
20
60
100
140
180
Temperature °C

Fig. 3.8

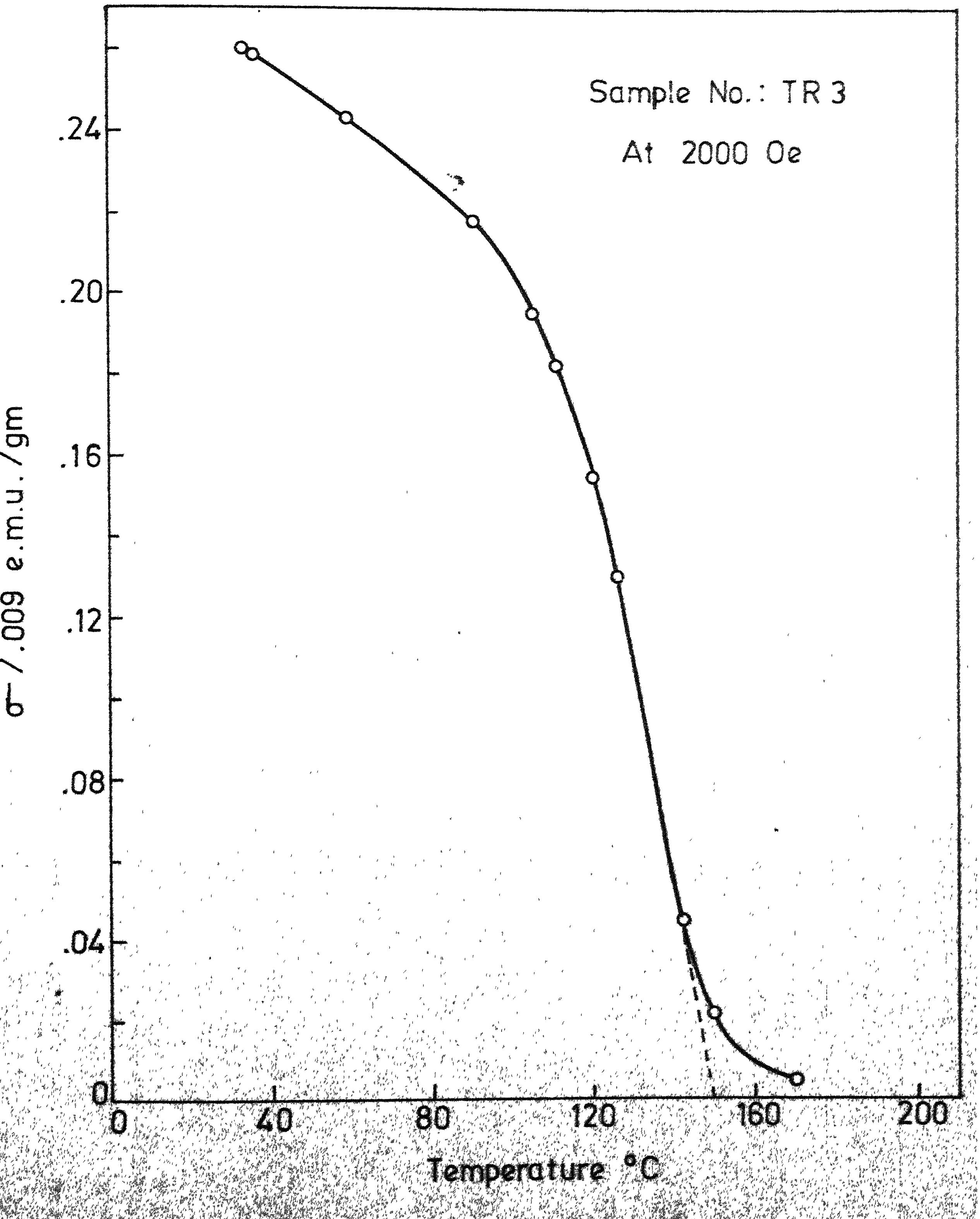
Sample No.: TR 3
At 2000 Oe
σ /.009 e.m.u./gm
.24
.20
.16
.12
.08
.04
0
0
40
80
120
160
200
Temperature °C

Fig. 3.9

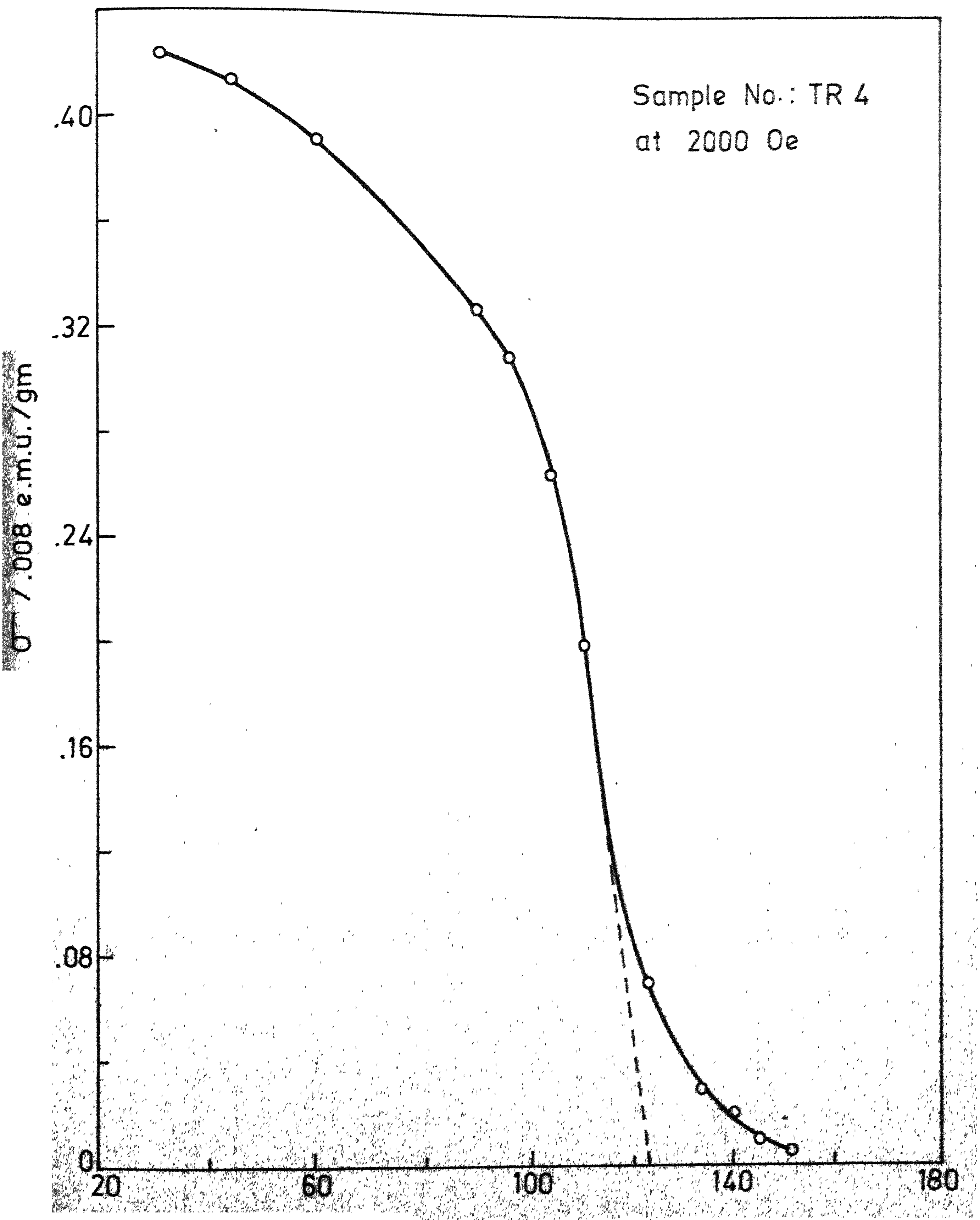
Sample No.: TR 4
at 2000 Oe
σ / .008 e.m.u./gm
.40
.32
.24
.16
.08
0
20
60
100
140
180
Temperature °C

Fig. 3.10

of Sb_2O_3 (1%) (TR2) some what increases the coercivity and saturation magnetization over the values obtained for the sample TR1 without the addition of Sb_2O_3 . Also it is seen that addition of 5% Fe (TR3) with the sample TR2 composition further increases the coercivity but reduces saturation magnetization. Again, 5% Co addition (TR4) increases the saturation magnetization further than for sample TR3. But 5% Ni (TR5) decreases the coercivity to a value lower than the values obtained by 5% Fe and 5% Co additions. Shannon et al[70] found that addition of Fe^{3+} ions decreases σ_s monotonously with increasing Fe contents. This is attributed to the fact that increase of Fe content increases the 'a' value and thereby changes the exchange force between the chromium ions. Also they found that addition of Fe^{3+} ions in excess of .2 wt % reduces the particle size and thereby increases the coercivity. It is seen that saturation magnetization for TR5 is higher than for TR3. Therefore, from the above Table the inference may be clearly drawn that additions of impurities such as Sb_2O_3, Fe, Co and Ni increase coercivity and saturation magnetization. Of all the impurities added, 5% Fe gives perhaps the best results. This is also borne out by our Curie temperature measurement, to be reported in the next section. Literature values also agree with this result. However, samples TR1 - TR5

could not attain the values obtained by the pure CrO_2 (A1) because of the presence of Cr_2O_3 phase. So Cr_2O_3 phase is considered as an impurity phase and it is concluded that this phase affects the magnetic properties of CrO_2 very sharply. But if we calculate the saturation magnetization and remanence magnetization only for CrO_2 phase the same way as Guillaud et. al[83], our value also expected to be substantially larger than the one reported in Table 3.4.

From the σ Vs temperature plot, we can know the onset temperature (Curie temperature, T_c) at which the magnetization vanishes. Table 3.5 shows the Curie temperature for different samples.

Table 3.5

Sample No.	Curie temperature (T_c) $\pm$ 2° C
A1	128
TR2	125
TR3	150
TR4	123

Curie temperature (T_c) of CrO_2 is important in magnetic tape applications. Low Curie temperature is characterized as a poor quality of tape recording materials. If the temperature increases so as to reach the Curie temperature of a magnetic tape recording material, the ferromagnetic state will vanish at T_c . So if T_c is very low, it will have a serious effect on magnetic tape recording properties since a slight increase in temperature during transportation or storage will lead to accidental erasure of previously recorded information on the tape. So, high Curie temperature is desirable for magnetic tape applications. Here, the effect of additives on Curie temperature is explored.

From the Table 3.5 , we know that T_c for pure CrO_2 (A1) is 128° C. Addition of 1% Sb_2O_3 (TR2) reduces the Curie temperature from 128° C to 125° C and addition of 5 wt % Co (TR4) still reduces T_c to 123° C. It is found that addition of 5% Fe increases the Curie temperature from 128° C to 150° C. Hirota[69] et al already found that upto 3.9 wt %, the addition of Fe increases the Curie temperature from 116° C to 154° C and after that it becomes constant for any further addition of Fe corresponding to 'a' axis expansion. This result suggests that solubility limit of Fe^{3+} ions exists in the range between

2 wt % and 4 wt %. Also, Shannon et al [70] found that addition of 2 to 5 mole percent Sb_2O_3 and Co_3O_4 decreases the T_c further. Our experiment results are therefore in excellent agreement with the literature values. It is found that the presence of Cr_2O_3 phase does not affect the Curie temperature at all.

CHAPTER IV

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The following conclusions may be drawn from the results of the present work.

(1) Acicular shaped CrO_2 alongwith a considerable amount of Cr_2O_3 phase was prepared from a mixture of CrO_3 and KNO_3 with and without the Sb_2O_3 , Fe, Co, Ni as additives. The method used required straight forward and in-expensive procedures without the use of high pressure.

(2) The maximum yield of CrO_2 has been obtained (calculated from weight loss of CrO_2 when heated in air - DTA, TG analysis) for 5% added Co by weight. However, if the presence of Cr_2O_3 phase is avoided, the yield would have been more than the observed value.

(3) The presence of additives such as Sb_2O_3 , Fe, Co, Ni reduced the particle size considerably.

(4) Magnetic measurements showed that the decrease in particle size enhanced the coercivity.

(5) Curie temperature measurements showed that the presence of 5% Fe increased the T_c from 128^o C to

150^{0} C and the presence of 1% Sb_2O_3 , 5% Co decreased T_c from 128^{0} C to 125^{0} C and 123^{0} C, respectively.

Based on the findings of this work, the following suggestions may be made for future studies:

(1) To avoid the presence of Cr_2O_3 phase, the batch composition and temperature may be varied and the optimum conditions may be thus explored.

(2) Instead of using a mild steel container, a mild steel container coated with nickel or chromium, or a stainless steel container may be used because mild steel container contaminates the starting materials in the presence of high temperature.

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